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COMPENDIUM OF NITROMETHANE DATA RELEVANT TO THE TACTICAL EXPLOSIVE SYSTEM (TEXS) PROGRAM

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A comprehensive search of the literature was conducted on nitromethane and hazards associated in its use. Each reference was reviewed and a summary provided. These summaries were grouped into the categories: adiabatic compression, detonation, tests, change in properties, health hazards, and problems associated with use in the Tactical Explosive System (TEXS). A guide to the use of the compendium and suggestions for research are included. Keywords:

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INTRODUCTION

The Tactical Explosive System (TEXS) is a system to create a ditch 12 to 13 meters wide by 3 to 4 meters deep for lengths of approximately 300 meters. This is achieved by emplacing a pipe in the soil, filling it with explosive, and detonating it. Nitromethane (NM), a liquid explosive, is under consideration as the explosive for the system. The TEXS program would then involve handling, shipping, and storing of large quantities of NM and possible unloading later. An evaluation program of a system using NM must be conducted to determine whether specifications for the system can be met. Any hazards, that may be encountered, must be identified.

NM has been extensively studied because it is a clear liquid serving as a prototype homogeneous explosive; insensitive when pure; sensitized by particular additives; capable of undergoing low velocity detonation associated with precursor waves as well as high velocity detonation; a relatively simple organic molecule; suitable for studying mechanisms involved in initiation by different sources. Therefore, there exists a large body of literature on NM. The TEXS program urgently required answers to many questions pertinent to the use of NM. If an NM system were selected, there would be a continuing need for an up-to-date body of relevant information. In conjunction with the evaluation program already underway, the cognizant personnel at the Armament Research Development and Engineering Center (ARDEC) arranged for this scientific services program with the following tasks.

a. Prepare a compendium of information on NM appropriate to TEXS operations which includes information on potential hazards and such other information that the researchers deem pertinent.

b. Evaluate the validity of the information in the compendium.

c. Prepare suggestions for research that would fill any gaps in the knowledge required for safe operations.

The information gained from these tasks would provide a body of knowledge readily available to those already involved with TEXS and also serve as an introduction to those entering this field. In this way, it would not be necessary for each individual to conduct his own search for information and progress to the forefront of the field would be accelerated. This compendium is to serve TEXS' needs, not to provide a general review for all the extensive NM literature.

APPROACH

A "compendium is a summary or abstract containing the essential information in a brief form; concise but comprehensive treatise" (dictionary definition). To this end, the compendium provides access to successively more detailed information at the option of the user.

The development of the compendium began with extensive literature searches. The libraries at Picatinny Arsenal and Los Alamos National Laboratory were the primary sources. Reports by manufacturers, sponsored reviews, and other TEXS documents were made available by the TEXS team. Computer searches were made through DTIC, NTIS, and DIALOG. Library card files were reviewed for relevant headings. Chemical Abstracts and other indexes were used. Knowledgeable scientists and engineers in the field of explosives were contacted for guidance to important material or to provide copies of otherwise unavailable references. The background of the authors also led to inclusion of important material and facilitated contacts with key personnel. Over a thousand potentially pertinent references were found. These were individually screened first by title and then by abstract. The source material for the compendium was selected in this way.

To organize the source material a set of categories was devised so that each category would contain a large number of the references. Individual references could contribute to more than one category. In such cases, they are included in each category. Thus, if the user is interested in a particular area, it is not necessary to pursue the subject beyond the designated relevant category or categories. The categories, with a brief description of content, are listed below.

Category 1 -- Adiabatic Compression: It is well known that the presence of voids, inert particles, ullage and/or cavitation serve to sensitize NM when a pressure wave is applied. The parameters that govern this sensitization and the behavior for various loadings, experimental and theoretical, are to be found in this category. Low velocity detonation insofar as it depends on adiabatic compression is included here.

Category 2 - Does not exist at this time. It is reserved for possible future need for a separate category dealing with ignition and burning exclusive of that caused by adiabatic compression and not leading to detonation.

Category 3 -- Detonation: NM undergoes high-velocity detonation directly when pure, or can run-up from low-velocity detonation or an adequately strong shock when sensitized by "hot spots" or additives. Thus, topics such as critical diameter, effect of density, temperature, run-up, and the like relevant to detonation are included in this category.

Category 4 - TEXS Problems: Specific descriptions, analyses, specifications, problems, solutions that relate directly to the TEXS system are in this category. There is considerable overlap with the other categories because work in this category requires knowledge of the others. The use of this category is described further in the next section on GUIDE TO USE OF THE COMPENDIUM.

Category 5 -- Health Hazards: Working with NM requires data on toxicity, allergic reactions, personnel protective devices, environmental impacts, and effects of contaminants and impurities.

Category 6 - Tests: Techniques for evaluating sensitivity in different situations and methods for assessing significance of test results including modeling as applicable to the TEXS program.

Category 7 - Changes in NM: Pure nitromethane has physical and chemical properties that change with temperature, pressure, aging, contaminants, impurities, re-use, fungus, etc. A compilation of existing data is needed to support the other categories and for direct use in the TEXS program.

Each reference included in this compendium was reviewed. A summary was written on a 5 x 8 inch index card whenever feasible and extended when necessary. These summaries could not replace a full reference (some had fifty or more pages). The thrust in the summary was to provide guidance to content, relevance to TEXS, and abstract key information of particular value. As the reference was reviewed to satisfy Task 1, Task 2 comments regarding validity were included. This approach permitted immediate connection to more recent references or data. It was possible to note in the summary that particular parameters were not included, reducing the value of an analysis, etc. Hence, the summaries of the references were designed to satisfy Tasks 1 and 2 simultaneously.

The summary sheets, a set for each category, are not all alike. In each case, the approach has been made appropriate to the material reviewed. The differences are covered in the next section on GUIDE TO USE OF THE COMPENDIUM. (The summary sheets were supplemented at ARDEC only by copies of almost all the references. In this way the compendium can serve the ARDEC user in the area of interest to the level required.)

GUIDE TO USE OF THE COMPENDIUM

The summary sheets are numbered as follows:

Category 1, Adiabatic Compression--1 through 94, future use to 199
Category 2--Reserved for future reallocation from categories 1 and 3 for deflagration
Category 3, Detonation--301 through 390, future use to 399
Category 4, TEXS--401 through 419, future use to 499
Category 5, Health Hazards--500 through 526, future use to 599
Category 6, Tests--601 through 653, future use to 699
Category 7, NM Changes--700 through 789, future use to 799

In some categories, a few numbers have been left vacant so that related material can be entered adjacent to other relevant material already in place. This is in accord with use as a loose-leaf compendium and floppy disk storage for easy updating.

For the reader who is being introduced to the TEXS program, a description of the system may be found in 401. The problems that arise are also in this category. Item 411 is an analysis that illustrates use of the compendium to cope with one problem, namely the need for a nitrogen blanket. Item

3

408 also draws on the compendium for the formulas used therein and does calculations on the hydraulic-hammer hazard that resulted in a change in the test design for qualification, as seen in 409 and 410.

For the reader particularly concerned with health hazards, an introductory summary on toxicity, environmental impact, and personnel protection has been provided as number 500. After reading this summary the individual references in this category may be pursued.

For the reader requiring data on NM properties, a summary is provided as number 700. In this case, an index for specific properties is included with the summary. Similar summaries may be added at a later date for Categories 3, 4, and 6 as numbers 300, 400, and 600. None is envisioned for Category 1 because of the extremely large scope of this topic. Adiabatic compression could be the subject of a separate major report in the preparation of which the compendium would significantly contribute.

Within each category an effort has been made to group the references with respect to mutual relevance. Thus, the contributions of authors from the same installation are together because very often the same equipment or computer program is used or one paper references the others as further progress is made. For example, numbers 13 through 19 are all from the Bureau of Mines on adiabatic compression of bubbles in liquid. This approach was facilitated by including the organization represented with the names of authors in the reference citation.

For convenience, when a paper or report is relevant to more than one category, the same summary is provided in each category and lists all relevant reference numbers. For example, in the paragraph above the Bureau of Mines numbers appear as 13/301, 17/302, 14/303, 15/304, 18/307, and 19/309 because relevance is present to both categories. However, 305 and 306 have been added which are appropriate to Category 3 but not to Category 1. Also, the numbers used for the Bureau of Mines contribution are chronologically arranged because there was a definite progression in the understanding of the low velocity detonation phenomena over the years.

There was a considerable contribution to Category 1 from the field of liquid propellants for the liquid-propellant gun. These were grouped together as numbers 27 through 36. References from the same country were placed adjacent to each other where mutual relevance existed. Except for Category 1, the foreign references followed the domestic references, and the Soviet literature was last in categories 3, 4, 6, and 7.

Each category is preceded by a list of the reference numbers that are summarized therein. This provides ready access to particular references or types of information.

The literature on nitromethane (NM) is extensive, as readily seen from this compendium. In general, the work represented was not directed toward the TEXS application. For this reason, it is necessary to supplement the compendium with additional research.

Adiabatic Compression

To assess the hazard of adiabatic compression of NM, it is necessary to know the values of the parameters that determine the threshold for ignition as a function of the state of the NM and the environments it is subjected to in the TEXS application. NM may age, become contaminated, cavitate, expand, crystallize, etc. It must be operable from -25°F to +120°F after storage at -50°F to +160°F. The storage drums must remain intact to +175°F. The NM will be pumped at rates leading to flow velocities ~ 20 fps and subjected to hydraulic hammer pressures ~ 300 psi. It is essential to know the relation of the operating situation for the worst case to the threshold for ignition. The threshold is known to depend on compressibility, density, viscosity, vapor pressure, surface tension, and thermal diffusivity of NM together with chemical reaction rates of the vapor in the presence of air and a nitrogen blanket. The value of all of these parameters over the operating range are needed to be fed into an applicable theory or computer program to predict the hazard and define a safe operating domain. Research to achieve this goal through use of an overall theory is not yet completely established. It is a worthwhile objective to use any results obtained, as described in the next paragraph, to extend and calibrate the referred-to computer program, and use it along with the to be described experiments for guidance, interpretation, and extrapolation to the TEXS problem.

It is necessary to measure pertinent properties of NM, to do adiabatic compression experiments, and determine the threshold for ignition. This has been done for the liquid propellant gun system as described in references 27 through 41. Therefore, the logical approach would be to make those determinations necessary to extrapolate/scale from the liquid propellant studied to NM for the changed operating environment.

One possible set of tasks to achieve this would be:

a. Provide data on physical properties of NM that are important to characterize hydrodynamic surge pressures during dynamic fill processes and to characterize bubble collapse processes appropriate to the operation of the TEXS over the range of -25°F to +120°F.

b. Conduct theoretical analyses of adiabatic compression phenomena of bubbles in NM using data from a above, then coordinate this theory or computer program representation and calibrate with results from c below.

c. Conduct lab-scale experiments on NM to establish the safe operating corridor for the TEXS application. In particular, identify all possible "worst case" scenarios that might be encountered.

d. Based on b and c, provide an engineering judgment on the hazards to personnel relative to adiabatic compression for TEXS using NM.

Detonation

The vulnerability of the TEXS to enemy attack requires evaluation when using NM. Here the threat is not loading and unloading, handling, etc. but is instead bullets, mortar rounds, shaped charge jets, incendiaries, etc. The greatest hazard is sympathetic detonation of an assembly of drums or any large quantity of NM (e.g., tank car). It is necessary to establish, by simulation-type experiments, which threats lead to sympathetic detonation. To support this determination, the requirements to detonate a single drum of NM should be found. Fundamental experiments on pure NM and NM with bubbles, contaminants, etc. are also needed to see if low-velocity detonation occurs and what critical dimensions and confinements are required to initiate high order detonation directly and by transition from low-order detonation.

Health Hazards

A major impurity in NM is 2-nitropropane (2-NP); its OSHA threshold limit value for inhalation of vapor in air is 25 ppm (90 mg/m^3) (Refs. 506, 513, 515, 516). Different batches from different suppliers contain varying amounts of impurities. The OSHA/Federal limit value for NM vapor inhalation of 100 ppm/8 h in air has been found adequate, but no data seem to exist on the influence of 2-NP with its 25-ppm limit. For NM materials specification, it might be desirable to determine the maximum amount of 2-NP allowable in the product. 2-NP has been identified as a potential carcinogen (Refs. 505, 512, 513, 515).

Environmental effects need to be quantified. NM decomposes in the atmosphere, but no amount/h limit seems to be available (Ref. 530). The related OSHA limit value of 100 ppm/8-h day should be reevaluated for NM with various impurities (Ref. 504). A safe limit has been established in the USSR as 0.005 mg/L but no information was located on US tests (Ref. 527). Percolation tests should be done at different concentrations. An overall evaluation should be made of the pollution of soil, air, and water resulting from TEXS and the resulting health hazards (Refs. 516 - 526).

Other questions, for example on aging and storage, remain to be answered because no data are available in the literature (ref. 506).

Tests

The conditions for a worst case scenario simulating TEXS use in the field needs to be established. A simple test of NM to establish that the liquid has not been sensitized is needed for use by soldiers in the field prior to use and particularly if the NM has been removed from the pipe and stored.

Changes in Nitromethane

Different batches of commercial NM from different suppliers contain varying amounts of impurities. The major impurities identified were nitroethane (NE), 2-nitropropane (NP), propionitrile, and water (H_2O). Propionitrile and NP are potential poisons and can explode on heating (Refs. 504, 505, 510-518). Propionitrile, found more often in non-US commercial product, has been found very difficult to eliminate (Refs. 727, 745, 766). Pure NM was found more compatible with storage materials than was commercial NM. No comparative data were found on health or explosion effects of mixtures with different percentages and combinations of impurities. It would be desirable for materials specifications and safety reasons to determine the allowable limits for impurities in commercial NM.

The effects of contaminants are not known because the contaminants and how they enter the system have not been identified. Impurities (see above) might qualify as contaminants at certain concentrations/percentages.

Certain catalysts promote detonation. Certain decomposition products are more sensitive than NM alone, but no safety limits seem to have been established.

Another concern about NM is its behavior at low temperatures, where it changes from liquid to solid, then melts again. Questions on changes in sensitivity, on impurities/contaminants that may react differently under these conditions need to be answered. The temperature/pressure equations can, in some instances, be extrapolated.

Research is required to establish the range of physical and chemical behavior of NM for the TEXS application. (See Adiabatic Compression above.)

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CATEGORY 1

ADIABATIC COMPRESSION

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"Adiabatic Thermal Explosion of Entrapped Gas in Liquids," Yu. M. Volynskii-Basmanov and V. I. Kuz'min, Combustion, Explosion and Shock Waves, 4, No. 1, pp 29-31, 1968.

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"Initiation and Development of Detonation as a Result of the Action of Weak Shock Waves on Liquid Explosives," A. V. Dubovik and V. K. Bobolev, <u>Combustion, Explosion and Shock Waves</u>, <u>5</u>, No. 3, p 245, 1969.

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"Sensitivity of Some Explosives to Shock Wave," V. S. Ilyuklin and P. F. Pokhil, Dokl. Alad. Nauk., SSSR, <u>140</u>, pp 179-180, 1961. C.A. <u>56</u>, 6229H, 1962.

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"Critical Energy of the Excitation of an Explosion by Impact in Different Explosives," M. Ya. Vasil'ev, Detonatsiya, Mater. Vses, Simp. Goreniyu Vzryvu, 6th Edition, Dremin A. N., pp 65-68, 1980, In Russian. Publisher: Akad Nauk SSSR Inst. C.A. 95:100043w

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"Study of Hydraulic Shock in Hydrodynamic Shock Tubes," B. E. Gelfand, E. I. Timofeev, Inst. Khim Fiz, Moscow, USSR, Teplofiz Vys Temp 1983, 21(2), pp 330-334, In Russian. C.A. 99:7468m

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"Development of a Reaction in Compression-Loaded Nitromethane and Tetranitromethane," A. A. Vorob'ev, Fiz-Khim Protessy Gazov. Kondens. Fazakh Editor V. N. Kondrat'ev, 109 pages, 1979, In Russian. Publisher: Akad Nauk SSSR, Inst. Khim Fiz. Chernogolovka, USSR. C.A. 93:149526d

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"Kinematics of a Gas Bubble in a Liquid in the Presence of a Strong Acoustical Compression Wave," Yu. P. Grebenkin and V. M. Kryachko, In Russian, English abstract in Vestn. Leningr Gos, Univ, Ser Fiz Khim <u>22</u>, No. 4, 79, 1978). C.A. 90:12796c

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"Influence of Gas Density upon Splitting of Gas Bubbles," B. E. Gelfand, S. A. Gubin, R. I. Nigmatu, Academy of Sciences USSR Proceedings, In Russian, Dokl. Akad Nauk SSSR, 235, No. 2, 292.

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ADIABATIC COMPRESSION

1

"On the Pressure Developed in a Liquid During the Collapse of a Spherical Cavity, Lord Rayleigh, O.M., F.R.S., Philosophical Magazine, 34, pp 94-98, 1917, available in Collected Papers, 6, pp 504-507.

This is the first comprehensive treatment. Assumes fluid to be incompressible. However, as pressure rises near origin includes compressiblility and believes that earlier neglect of compressibility does not greatly affect results. States "for a satisfactory theory compressibility would have to be taken into account at an earlier stage." JH: This was done by the Ben Reuven and Summerfield (PCRL) work (32)(33).

Approach is to equate the work done in an increment of compression to the change in kinetic energy of the fluid that corresponds. Finds the time of collapse to a given fraction of the original radius as proportional to R_0 $\rho^{\frac{1}{2}} p^{-\frac{1}{2}}$ where ρ is the density of the fluid and p is the pressure at infinity. Equation 5 gives t vs R/R_0 and Equation 6 gives τ, for complete collapse as 0.91468 $R_0 [\rho/P]^{\frac{1}{2}}$. With Q initial pressure Z = R^3/R_0^3. Includes gas pressure and shows oscillation will occur. Gives table of P/Q versus Z. JH: One should work through this for the action of the parameters and as a base for further study.

2

"The Dynamics of Cavitation Bubbles, M. S. Plesset, Journal of Applied Mechanics, 16, Trans. ASME 71, pp 277-282, 1949.

Derives (Eq. 7) a general equation of motion for a spherical bubble in a liquid with given external pressure P(t) and with pressure at the bubble boundary p(R). Gets Rayleigh's solution as a special case. Concern is with cavitation formed bubbles and their evolution in a flow over a body. Includes vapor within the bubble. Notes that the "limitations of this equation of motion include the effect of the finite rate of evaporation and condensation, and compressibility of vapor and liquid." JH: Again, all factors are not included. In addition to those mentioned, asymmetry of bubble collapse and bubble aggregation can also be factors. Includes a cavitation

parameter $K = \frac{p_0 - p_v}{\frac{1}{2}(\rho V_0^2)}$ where p, p_v are static pressure and liquid vapor

pressure and V_0 is velocity of flow of density ρ. JH: One should ask whether the cavitation field literature provides information on possible cavitation at higher temperatures in the pipe as NM is loaded. States that small air bubbles can act as nuclei for formation of cavitation bubbles containing vapor. JH: Thus a small air bubble created in loading can grow with vapor in the flow.

3

"The Collapse or Growth of a Spherical Bubble or Cavity in a Viscous Fluid," H. Poritsky, Proceedings of the First U.S. National Congress of Applied Mechanics at Illinois Institute of Technology, Chicago, June 11-16, 1951, published by ASME, pp 813-821.

This paper is a mathematically elegant restatement of bubble collapse but with consideration given to the role of viscosity and surface tension of the liquid. Does special cases with numerical results, e.g., Figs. 7 and 8. **JH: Note that NM becomes viscous at the low temperatures extreme of the desired range. Assumes spherical symmetry, incompressible fluid.** Figure 3 shows large difference for collapse of a spherical bubble in viscous and non-viscous fluid. Figure 7 shows small differences in a viscous fluid due to surface tension for collapse.

4

"Note on the Collapse of a Spherical Cavity in a Viscous Incompressible Fluid," S. S. Shu, Proceedings of the First U.S. National Congress of Applied Mechanics at Illinois Institute of Technology, Chicago, June 11-16, 1951, published by ASME, pp 823-825.

This paper rigorously establishes the results obtained by numerical integration by Poritsky (3) at the same meeting. A dimensionless parameter c of viscosity is found to play an essential role. The time of collapsing is infinite if c is greater than a critical value and is finite otherwise. When surface tension is included, the time of collapse is always finite. **JH: As Poritsky does, here too fluid is incompressible, spherical symmetry assumed. Further considerations for real fluids are in later papers by R. Plesset (5), Din-Yu Hsieh (7), and then one should look at the PCRL treatment (32)(33). It becomes clear that experimental studies for each particular case are essential since the theories involve parameters and assumptions for which values and validity respectively are not established.**

5

"Bubble Dynamics," Milton S. Plesset, Cavitation in Real Fluids, edited by R. Davis (Am Elsevier, Pub), pp 1-18, 1964.

Dinstinguishes between vapor bubbles (essentially no permanent gas) and where permanent gas greatly exceeds the vapor-gas bubbles. In both cases surface tension is involved. Recognizes, but does not include, the importance of the compressibility of the liquid. Thermal heating of the bubble arises first (vapor-containing) from the heat of condensation and second from the fact that the condensation eventually cannot keep up with the interface motion. The vapor then is heated by compression like a permanent gas. The spherical shape of the collapsing bubble becomes unstable and the bubble will break up as a consequence. For a slow process, there is sufficient time for heat to be conducted away so as to maintain the isothermal condition, whereas

for a fast process the adiabatic condition applies. Does special case of air-bubble in water. Has a section on bubble stability and does an example to show how to determine ripple limit on stable size of an oscillating bubble. **JH: This paper is one more in the sequence starting chronologically with Besant, Rayleigh (1) delineating role of factors involved.**

6

"Some Analytical Aspects of Bubble Dynamics," Din-Yu Hsieh, Journal of Basic Engineering, pp 991-1005, Transactions of the ASME, December 1965.

This is a comprehensive treatment. Adds the consideration of assumption of a uniform interior of the bubble. Various aspects of the problem are investigated depending on whether the thermal, inertial, or diffusive effect dominate. Non-linear mechanical oscillations are discussed as well as linear with thermal and diffusive interactions. The paper concludes with a study of the stability of the spherical symmetry of the flow system. Notes that the following remain to be studied: collapse of a non-uniform bubble, compressible fluids, nucleate boiling, forced non-linear oscillation, stability, non-spherical bubbles. **JH: With the complexity of the theory to this point (1917 - 1965) and the important features still not included, it was clear that the best way to proceed was to do experiments that simulated the situation of interest with real fluids. Succeeding references do this until PCRL does a comprehensive theoretical study (still not a complete representation). (32)(33)**

7

"Sensitivity of Explosives VIII, The Effect of Compression of Occluded Gas Bubbles on the Initiation of Liquid Combustibles," Jules W. Enig, NAVORD Report 6093, June 2, 1958.

In this paper the governing differential equations are solved directly by a computer program. Reaction of the vapor as a step function is included. Concludes that for all other boundary conditions equal, it is possible for a smaller bubble to reach the same maximum temperature and pressure as the larger but in a shorter time so that a smaller bubble may initiate a liquid combustible while a large one will not. Assumes in his approach that no thermal conduction, vaporization, or condensation takes place at the bubble wall. Also assumes spherical bubble and incompressible liquid and monomolecular chemical reaction. **JH: The conclusion with respect to most hazardous bubble sizes is not correct in general. It may be considered to be the result of his assumptions. The value of this paper is in the introduction of a chemical step providing a change in adiabat and in numerical solution by computer of governing equations instead of seeking analytical solutions.**

25

"Investigation of Low-Velocity Detonation Phenomena in Liquid Propellants, Fuels and Explosives," D. C. Wooten, M. Cowperthwaite, and D. C. Erlich, SRI Final Report, June 30, 1972, SRI Project SCU-7771. (Includes "Collapse of a Vapor Bubble Leading to Hot-Spot Initiation," David C. Wooten, March 1972.)

Hot spot initiation by a bubble due to both shock focusing and micro-jetting are generally of interest for shock strength in excess of 50 KBar. Low velocity detonation associated with cavitation model. [See BuMines (13) - (16).] Includes the effects of both heat and mass transfer (vaporization) at the bubble wall. Assumes no viscosity for liquid and temperature equalization, uniform interior, spherical bubble, stationary bubble, incompressible liquid. Sets up and solves the equations. **JH: He does the problem for the simplifying assumptions which are NOT the true case. The value of the paper is the excellent review of the subject to date with 27 reference citations and some techniques used, such as the dimensionless variables chosen. Experiments are clearly required to support or refute theories.**

9

"Investigation of Low-Velocity Detonation Phenomena in Liquid Monopropellants and Explosives," M. Cowperthwaite and D. C. Erlich, SRI Final Report, February 1974, SRI Project PYU-2383. (Includes "Calculation of the Collapse of a Vapor Bubble Leading to Hot-Spot Initiation," Jay Levine and D. C. Wooten.)

This paper differs from the previous appendix by D. C. Wooten alone by following eq. 8 with a statement of the equations to be numerically integrated, transforming them and generating a finite difference solution. [The previous paper has the detailed review of previous studies and a particular small-time solution (8).] Concludes, "In general, larger bubbles and higher overpressures lead to earlier ignition (in terms of bubble radius)." Recognizes need "for the solution of the rebounding bubble, which requires liquid compressibility, and finite rate kinetics." **JH: As stated in the previous paper (8), this work also has a domain limited by the assumptions made.**

10

"Cavities and Munroe Jets in Liquids: Their Role in Explosion," F. P. Bowden, Nature, 206, pp 380-383, April 24, 1965.

Hot spot can result from adiabatic heating of the compressed gas or by reinforcement or deflection of the shock wave at a discontinuity. A shock wave acting on a bubble in a liquid may produce a Munroe Jet. The jet impact produces a high pressure and temperature. **JH: Note that except for symmetrical bubble collapse, a shock is required for other mechanisms.** Experiments done with a flat glass hammer striking nitroglycerin on a flat glass anvil demonstrated the role of Munroe jets as contributing to the initiation. Note also that a pressure wave reflected from a liquid surface

cavitates the liquid forming bubbles. JH: Shock (compression) waves are formed when a liquid column is abruptly brought to rest at an obstacle. Tension (release, rarefaction) waves form when the compression reaches a free surface. The phenomena described were observed from impact sensitivity tests. JH: The greater importance of intensification at discontinuities and Munroe jets is for low velocity detonation in a liquid. [See BuMines papers (13) -(16) and those of LANL (18) - (20).]

11

"The Detonation of Liquid Explosives by Gentle Impact. The Effect of Minute Gas Spaces," F. P. Bowden, M. F. R. Mulcahy, R. G. Vines, and A. Yoffe (GB), Proc Roy Soc, 188A, pp 291-311, February 1947.

Attributes the impact sensitivity (drop hammer test) to presence of minute gas bubbles. "These tiny gas bubbles (the mass of bubble may be about 10^{-10} g and its volume at atmosphere pressure about 10^{-7} cc) are heated by adiabatic compression and initiate the explosion." Work was done on nitroglycerin. Nature of surface of entrapment between anvil and hammer are shown to be important.

JH: This is an early paper. Applies particularly to very small quantities of liquid in the drop hammer test and only for nitroglycerin. Later studies showed that stagnation of liquid between anvil and hammer led to high temperatures promoting ignition with bubbles still playing a role. One should not conclude that a limited number of microscopic bubbles in NM would seriously sensitize it in the TEXS application.

12/341

"The Initiation and Growth of Explosion in Liquids," G. D. Coley and J. E. Field, 9th International Congress on High Speed Photography, August 2-7, 1970, Denver, Proceedings SMPTE, pp 466-473.

The transition from deflagration to a low velocity detonation was found to depend on the production and collapse of cavities in the liquid ahead of the reaction front. JH: Note that if liquid has the distributed bubbles due to another cause, e.g., previous cavitation, then ignition at one site would rapidly lead to low velocity detonation. Reviews work of authors pertinent to role of cavities. Photographed the role of cavities interacting with a deflagration front. A cavitation front first creates the bubbles and then the deflagration front moves in and a transition in velocity of propagation follows. Used primarily nitroglycerine. The transition depends on the adiabatic collapse of bubbles in the liquid ahead of the reaction front. JH: The energy intensifier profile is the determining factor on the transition from deflagration to detonation; it also applies for LVD to HVD transition.

13/301/635

"Initiation and Growth of Detonation in Liquid Explosives, F. C. Gibson, C. R. Summers, C. M. Mason, and R. W. Van Dolah (BuMines), Third Symposium on Detonation, pp 436-454, 1960.

Begins with a summary with reference citations of possible alternate mechanisms to adiabatic compression of contained gas. Did initiation and growth studies in liquid explosives (with test configuration shown in Fig. 1) by shock excitation. Configurations and wall materials were changed in a form of card gap test. Proposes mechanism for initiation of detonation in liquid explosives as cavitation established by shock excitation, possibly with additional heating of the liquid provided by shear forces resulting from differential particle velocities in the liquid and between the liquid and container walls. For a high intensity stimulus, gas bubbles will be formed from the dissolved gases which may first exist as small invisible bubbles of microscopic dimensions. These bubbles, finely dispersed throughout the liquid, constitute weak points as the tensile strength is determined by the largest bubble present. In addition, impurities such as dust particles provide nuclei as do small imperfections in the wall. During cavitation small bubbles may coalesce into larger bubbles of a size sufficient for compression to result in adiabatic heating. Any decomposition of the vapor or droplets in the bubbles which results in the production of gas also results in an increase in bubble size. The time required for the foci to grow through coalescence and reaction may well account for the long delays observed in this initiation process. JH: The sequence describing the role of bubble formation and growth is equally applicable to the point where a stimulus acts on the larger bubbles or created ullage. Whether ignition occurs then depends on the profile of the stimulus and the reactivity of the vapor and liquid as well as the thermal conductivity of both gas, vapor, and liquid and mechanical properties that modulate the adiabatic compression into oscillations at particular rates of compression. For the low velocity detonation model in which the wall carries a precursor shock producing cavitation, the speed of disturbance in the wall material and as a pipe should be established by literature or experiment. This must be compared with velocity in NM and impedances of NM and wall to determine whether a precursor could exist. For performance, one would think that high velocity detonation is desired. However, for cratering, it may very well be that low velocity detonation would be more effective. The selection will depend (if low velocity detonation is feasible) on the mode of initiation. [See (14).]

14/303/636

"Detonations in Liquid Explosives - The Low Velocity Regime," R. W. Watson, C. R. Summers, F. C. Gibson, and R. W. Van Dolah (BuMines), Fourth Symposium (International) on Detonation, pp 117-125, 1965.

Begins with a summary with reference citations to earlier work on low velocity detonation. Figure 1 provides the geometry for study of low velocity detonations. "Interest in the low velocity phenomenon has developed following recognition that these abnormal detonations play an important part

in characterizing the hazards of liquid explosive systems, as demonstrated by the too frequent accidents that have occurred in NG and liquid monopropellant facilities from relatively mild stimuli." LVD "can be initiated by pressures one or two orders of magnitude less than that required for HVD." Concludes "that perturbations of the liquid resulting from precursor wall waves exert a strong influence on the subsequent reactions." For an observer that moves with the reaction, the sequence of events can be visualized as: (a) undisturbed liquid compressed by bow waves derived from the precursor wave in the wall; (b) the compressed fluid begins to move outward where the wall moves outward; (c) liquid cavitates; (d) cavities grow until encounter shocks near reaction zone; (e) cavities collapse, generating high pressures and associated temperatures that are adequate to initiate chemical reaction. Model for LVD requires that shock velocity in wall be greater than in liquid for stable propagation. JH: Note that (b) depends on nature of wall; plastic wall moves out more and faster than steel. Also, need wall and liquid properties to support this mechanism.

Experiments using air-filled hemispherical cavities located on the free surface of fluids, as well as air-filled bubbles in a bulk of liquid explosive, indicate that liquid micojetting may be responsible for the initiation of reaction within the cavities. JH: For microjetting to be a viable mechanism, a shock must act on a bubble. Mader's work (314) used 95 Kbars; even two orders lower 0.95 Kbars, 950 atmospheres, would be far above pressures to be encountered by any water hammer scenario. This study used a tetryl donor acting through Plexiglas to produce a weak shock. Authors cite their work in R. W. Watson and F. C. Gibson's, "Jets from Imploding Bubbles," Nature, 204, 4965, pp 1296-1297, 1964. There they used a tetryl donor acting through 0.75-inch thick aluminum on a bubble in liquid. The pressure that acted was 10 Kbar. The pressure at jet impact was estimated as 100 Kbar. JH: Again note microjetting coincides with at least a weak shock, but could be important for transition process from LVD to HVD. LVD or HVD depends on initiating stimulus.

15/304/637

BuMines Quarterly Reports on Sensitivity of Propellant Systems, January 1, 1966 - March 31, 1966, Quarter #6, "Initiation Mechanisms," and April 1, 1966 - June 30, 1966, Quarter #7, "Theoretical Studies on Bubble Compression and Growth," PA U110 487.

Input pressure acting on bubble 1.5 Kbars, 1500 atmospheres. Found threshold for EGDN liquid with bubbles containing air, CO_2, and Argon. For latter threshold lower than 1.5 Kbars. A column of gas bubbles is injected into the liquid by means of a No. 27 hypodermic needle having an inside diameter of 0.007 inch. The gas bubble experiments show a trend toward higher sensitivity as the ratio of specific heats of the included gas is increased, which supports the contention that the heat generated by the compression of the bubble contents may be responsible for the reaction. JH: This conclusion is based on a simple model of bubble collapse and should be compared with the more comprehensive treatment of PCRL authors (32)(33). Also, see (68) regarding gas diffusivity.

29

The observation that some degree of reaction takes place below the thresholds suggests that the initial reaction takes place in the vapor and/or droplet field within the bubble. If the rate of release is great enough, the surface of the cavity could then be ignited resulting in a propagating reaction. The reaction would fail to propagate if the energy released was inadequate to compensate for the losses resulting from the heat transferred to the surrounding fluid and the work done in establishing the flow field around the expanding bubble. **JH: This balance is why the rate of bubble collapse (or oscillation) assumes so dominant a role.** Figure 3 shows the arrangement for studying initiation of liquids containing bubbles.

The second progress report provides a theoretical study on bubble expansion due to internal burning. Liquid is assumed incompressible—spherical symmetry used. Designates a volume consumption rate per unit area of bubble surface, u_c, and average molecular weight of products, w, and assumes both ideal gas EOS and isothermal behavior of uniform products within. Then treats special case of stability of bubble expansion versus five different consumption rate expressions. Finds that for greater than a 1.5 power in rate law stable expansion will occur. For LVD, consumption rates are far higher than studied here. For such high rates, expect that turbulence/breakup of liquid would accelerate consumption and lead to LVD to HVD transition. Recognizes that at high pressures, factors neglected or assumptions made would not be valid. **JH: Interesting approach to important role of kinetics in ignition and growth. Vapor concentration at high temperatures would alter burning rate.**

16/308/638

"Initiation of Detonation in Insensitive Liquid Explosives by Low-Amplitude Compression Waves," J. E. Hay and R. W. Watson (BuMines), Sixth Symposium (International) on Detonation, pp 115-123, 1976.

An experiment devised to simulate the development of explosive reaction in a large mass of cavitated liquid is described in which a massive steel piston is propelled into a container (diameter 10 cm) filled with a liquid explosive into which bubbles have been introduced. In this experiment, transition to "detonation" has resulted using nitromethane and other marginally detonable liquids at initial piston velocities of 24 to 90 meters per second. With further increase in scale size, abrupt accelerations of the order of those occurring in transport may suffice to produce explosion. **JH: This is closest to TEXS application.**

A mathematical model is described by which the hazard potential of deflagration-to-detonation transition in large masses of a reactive liquid subjected to cavitating conditions and pressure surges can be assessed from buring rate data or from small-scale experiments such as that described.

Begins with a critique of Chaiken (18) whose results tend to indicate that the possibility of LVD in NM is marginal. Attributes his result to the large value of the calculated cavitation rate constant which leads to

30

decoupling of cavitation and reaction processes. Describes test for development of explosive reactions in liquids by weak stimulus (<1 Kbar). Projectile driven by compressed air moves down a steel barrel (10.2 cm i.d., 3.3 m long). The minimum criterion for explosion is cylinder unfolded or in pieces, significant blast, and complete consumption of the liquid. Bubble field in liquid with diameters in the range of 0.05 to 0.2 cm and density 0.5 to 10 cm^{-3}. In earlier work it was found that for NM initiations could not be obtained with the highest velocity when only one or a few large bubbles were present. The impact of the projectile on NM at the highest velocity produces about 2.5 Kbars. The threshold velocity for NM was 24 ± m/sec. Comparison with other liquids, on the basis of thresholds and literature burning rates, suggest that those systems that have burning rates less than about 0.13 cm/sec at 11 MPa do not seem to explode at the highest velocity of this test, and those with rates substantially greater exploded at lower impact velocities. Value for NM = 0.27. **JH: NM does explode at 24 ± 2 m/sec if bubble profile is present.**

Presents a simplified model with incompressible liquid (considers value for less than a few Kbars), spherical symmetry, Abel equation of state, isothermal expansion, and some simplifying mathematical assumptions. Derives bubble pressure versus time as a function of parameters (Fig. 2). Finds development of explosive reaction is very sensitive to the burning rate parameter, somewhat sensitive to bubble dimensions and density and importantly with scaling upward. In Discussion, R. I. Solouklin suggests that effect of assymmetric collapse must also be taken into account.

17/302/639

"The Effect of Physical and Chemical Properties on the Sensitivity of Liquid Explosives," J. E. Hay, J. Ribonich, F. H. Scott, and F. C. Gibson (BuMines), Fourth Symposium (International) on Detonation, pp 412-425, 1965.

Some LVD's have a steady propagation rate well above sonic velocity in the explosive and produce well-defined shocks of the order of 5-10 Kbars. Other LVD's have a fluctuating propagation velocity well below the sonic velocity and produce pressurs of the order of 2 Kbars or less but no clearly discernible shock wave.

Bulk temperature rise inadequate, hence energy concentrators required. Each element of the liquid must be subjected to two distinct stimuli: a rarefaction which cavitates the liquid, and a shock which causes cavity collapse. **JH: The mechanism applies to local ignition by "water-hammer" compression which can then transform to LVD and possibly to HVD.**

Describes card-gap test for liquids including resistance type probe. Gives results for NM. At 25°C used schedule 40 steel pipe of normal size 1 ½ to 4 inches with 16 inch length except for 4 inch was 72 inches long. Variations of donor and temperature. Results were ambiguous as shown in Table 2. No appreciable temperature effect was found. Threshold gaps corresponded to shock pressures in NM of about 11.5 Kbars.

31

JH: In later papers, the role of the wall in producing a precursor cavitation wave in the liquid was defined. However, data is valid in showing threshold from non-initiation (NI) as 11.5 Kbars for shock initiation of liquid at 90°C. See (18).

18/307

"On the Mechanism of Low Velocity Detonation in Liquid Explosives," Robert F. Chaiken (BuMines), Astronaut Acta, 17, pp 575-587, 4-5 October 1972.

Abstract—On the Mechanism of Low-Velocity Detonation in Liquid Explosives. A theoretical description of low-velocity detonation (LVD) in liquid explosives has been developed, based upon a cavitation model of the phenomena. In this model, precursor waves cause cavitation of the liquid; the cavities are then shock-initiated by the advancing detonation front. The Chapman-Jouguet (C-J) condition of classical detonation theory has been extended to this case where precursor wave effects are important. In essence, it is shown that coupling of rate processes through a precursor wave limits the number of Hugoniot adiabat states that are accessible. Thus, the solution to the Rankine-Hugoniot equations for the steady-state detonation velocity involves a minimization of the velocity subject to the constraints imposed by the coupled rate processes.

For the case of LVD in liquid explosives, six rate processes are identified and treated analytically to yield an expression coupling the detonation pressure, extent of liquid cavitation, and wall shock attenuation rate. This expression, along with the applicable jump conditions for the cavitated liquid and an equation of state for the detonation products, yield a quantitative description of stable LVD.

Calculated detonation velocities, pressures, and stability conditions are in very good agreement with the available experimental data for nitroglycerin, ethylene glycol dinitrate, and nitromethane.

JH: This is a theoretical paper on role of precursor cavitation waves in producing low velocity detonation (LVD). Earlier papers develop the qualitative concepts and provide data. (16) disagrees with this one regarding NM and indeed states there is a hazard. Author believes Chaiken did NOT consider interrelation of reaction and cavitation regarding bubble properties.

19/309/640

"Effect of Cavitation on the Shock Sensitivity of Liquid Explosives," V. Krishna Mohan and J. Edmund Hay (BuMines), Seventh Symposium (International) on Detonation, pp 373-384, 1981.

Describes the gap test for cavitated liquids. Shock sensitization due to cavitation is observed for NM, the threshold shock pressure changes from 80 Kbars to 7 Kbars with cavitation added by air bubbles. Propagation velocity was about 2600 m/sec for cavitated liquid (uncavitated 6320 m/sec).

Shock sensitivity is affected by the γ value of the gas with NM. Higher threshold values are obtained with argon ($\gamma = 1.67$) and the reverse for propane ($\gamma = 1.13$) compared to those observed with air and nitrogen ($\gamma = 1.40$). Threshold gap values are enhanced with oxygen (even though gammas are about the same as nitrogen and air). Diluents such as benzene or acetone desensitize NM at low diluent concentrations. Tests were done that demonstrated that "gas bubbles govern the initiation characteristics of NM." Vapor pressure of NM is given as 30 mm.

Wall has role in creating precursor, but also governs time that the dynamic pressure is maintained in the reaction zone, cavitating to driving reaction to completion.

JH: All the qualitative features are brought together. Need gamma for high vapor content of NM. Note threshold for shock initiation and detonation velocities given for LVD and HVD.

20

"Initiation of Explosion in Liquids. Transient Pressures During Impact," P. Gray, Research (London), 2, Suppl 392-393, 1949; C.A. 43, 945e, 1949.

Reference not obtained.

21

"Influence of Entrapped Gas on Initiation of Explosion in Liquids and Solids," A. Yoffe, Proc Roy Soc (London), A198, pp 373-388, 1949; C.A. 44, 2243 g, 1950.

Initiation of explosion is of a thermal nature and is due to the adiabatic compression and heating during impact of trapped bubbles as evidenced by (1) decrease in sensitivity when small gas bubbles are eliminated, (2) decrease in explosion efficiency when γ is reduced below that for air

$$T_2 = T_1 \left(\frac{p_2}{p_1}\right)^{(\gamma-1)/\gamma}$$ [therefore lower γ means lower T_2], (3) the very short time from impact to explosion and the location of the point of initiation at a compressed gas bubble. Equipment used for impact experiments for photographic observation is described.

Experiments were conducted in which the initial gas pressure could be varied from 1 to 100 atmospheres. Explosion efficiency drops as pressure is increased. Difference of results for air and nitrogen shows that the chemical nature of the gas is important (gammas are about same). JH: Note regarding nitrogen ullage.

The value of γ appropriate to the sudden compression of a gas is not the value at room T and p. During compression γ depends on rate of pressure rise. JH: **Later studies showed that rate of compression is critical because transport of heat from bubble is time dependent and for high pressures and loading rates mechanical compressibility of liquid is a factor.**

22/605

"The Ignition of Certain Monopropellants by the Adiabatic Compression of Bubbles: Part 1: A Theoretical Analysis of Adiabatic Compression Effects Produced by Sudden Pressurization of a Liquid Column Containing a Vapour Space," P. D. Verschoyle (ERDE, GB), Report No. 13/R/58, March 1959, (AD 215075) [U68192].

Picatinny Arsenal U68192 Pt. 1. Pt. 2 is classified, but contains unclassified material included here as the paragraph below.

(U) The relation between the driving pressure and rate of pressure rise in a bubble will normally be so complex that in a practical application it will not be possible to calculate the conditions in a bubble. In order to determine whether ignition is likely, it will be necessary to make measurements versus pressure and rates of pressure rise close to application. JH: **Study was entirely on isopropyl nitrate, not NM. Value is analysis of U-tube apparatus and effect of parameters on adiabatic compression. This is an early, but valuable report. Many parameters of adiabatic compression are not considered.**

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Abstract: (U) A theoretical analysis has been made of the dynamic behaviour of an apparatus used to reproduce practical conditions in an investigation of the ignition of isopropyl nitrate by the sudden compression of a bubble containing a gas saturated with propyl nitrate vapour. The apparatus consisted of a U-tube containing liquid isopropyl nitrate, the vapour/air mixture being compressed in one arm of the tube when gas pressure was applied suddenly to the surface of the liquid in the other arm.

The peak pressure attainable in the closed arm of the tube, using an inert liquid, is shown to be dependent on a high power of the ratio between the pressure applied to the liquid surface and the initial pressure in the vapour/air space. Thus very high peak pressures result from quite moderate/ applied pressure.

The theoretical peak pressure is found to be independent of the mass of the liquid piston and of the diameter of the tube (which is assumed to be of constant cross-section throughout its length). It is also independent of the length of the vapour/air space.

Theoretical pressure/time and temperature/time curves are derived for several different sets of conditions, in order to study quantitatively the theoretical effects of several variables on the rates of adiabatic pressure and temperature rise in the vapour/air space. It is to be expected that the faster the temperature rise, the more nearly will truly adiabatic conditions

be attained in practice, since there will be less opportunity for heat to be dissipated.

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Table of Contents

23/343

"Role of Cavities in the Initiation and Growth of Explosion in Liquids," G. D. Coley and J. E. Field (Cambridge), Proc Roy Soc London, Ser A, 335, 1600, pp 67-86, 1973.

This paper provides extensive results and understanding on how bubbles and the stimulus profile together determine the ignition, consequent deflagration, and low velocity detonation in the liquid. In particular, the role of confinement and release waves from the liquid interface therewith is treated. The interaction of bubbles is significant as reaction in one bubble generates a flow into adjacent bubbles. Jetting in later stages is important. Cavity collapse must be rapid so that heat losses do not prevent adequate temperature rise for initiation, and the environment must last long enough for initiation to occur. Some decomposition can occur followed by quenching of further growth reaction.

"Shock Sensitivity of Liquid Propellants: The Exothermic Decomposition of Isopropyl Nitrate Under Rapid Compression," P. Beeley, P. Gray, and J. F. Griffiths, Seventeenth Symposium (International) on Combustion at the University of Leeds, England, August 20-25, 1978.

Goal is to quantify under what conditions of compression gas phase spontaneous ignition may be induced. A rapid compression apparatus is described that acts on gas bubbles. Compression and heating are of the order of milliseconds while dissipation of heat from the compressed gas takes tens of milliseconds so that the time scale for reaction is 1 - 50 msec. The vapor was diluted in N_2, Ar, CO_2, or air or combinations of these. **JH: Note that this measures the role of vapor from the liquid within the gas bubble. Hence it is important as NM has a high vapor pressure. (NM was not studied.)** As compressed gas temperatures increase, pyrolysis increases. In inert gas, only decomposition occurs; in air, oxidation is also important. **JH: Significant regarding nitrogen ullage.** Ignition occurs ony when oxidation augments the decomposition reaction. Recommends: (a) storage with no free volume, (b) inclusion of a volatile polyatome component ($\gamma \rightarrow 1$) in liquid to enter bubble, (c) fill and store with inert atmosphere. **JH: Avoid adding bubbles or cavitation or impact.**

25

"Maximum Bubble Size as Safety Factor in Bubble Resonance Explosion," C. O. Leiber (Germany, Chem Ing Tech, 50, 695, 1978. In German.

Describes a bubble resonance that is size dependent such that if the size is above a critical size, adiabatic compression leads to ignition, deflagration, and possible transition to detontion. **JH: These two pages should be translated. See other work by some authors in English [(26) and (354)].**

26

"Approximate Quantitative Aspects of a Hot Spot. Part II-Initiation, Factors of Safe Handling, Reliability, and Effects of Hydrostatic Pressure on Initiation," Carl-Otto Leiber (F.R.G.), Journal of Hazardous Materials, 13, pp 311-328, 1986.

An order of ratios of chemical sensitivity for a constant size (1 cm) air bubble is of the order of NG/DEGN/GDN/NM $\approx$ 1/2/3/> 22 based on energy of falling weight and power into liquid (Table 2). Concludes that it depends on experimental conditions whether chemically caused differences are present. States that more viscous explosive is less sensitive. **JH: This is not always the case.** Dissolved gases change the viscosity, density, and compressibility of liquid. Infers that this could be a factor in difference sometimes observed for air and nitrogen pressurization. **JH: This is a new viewpoint on the reasons for using a nitrogen ullage.** The appendix provides

a thermodynamic approach to tne pressure dependance of the specific heat. JH: It has been recognized that the ideal gas value of γ changes for a pressure pulse and γ actually affects temperature in the bubble.

27/603

"Detonation Sensitivity of Bubbly Liquid Propellant for Guns," L. C. Elmore, R. N. Boyd, L. J. Gee, and G. C. Quinn (PSI), 16th JANNAF Combustion Meeting, Vol I, pp 285-326, September 1979.

Loaded a transparent chamber. Caviation occurred in the inlet passage resulting in a fine bubble structure. Water hammer pressure (approximately 1300 psi) completely changed the bubble structure in the chamber causing bubbles to disappear or become extremely small. When chamber pressure was dropped to ambient, the expanded bubbles were estimated to be no larger than 0.003 inch diameter.

Did modified card gap tests to determine the sensitivity of bubbly propellants to strong shock stimuli. The applied shock was supported by reaction in the liquid, but a detonation did not occur—a sustained velocity of 2430 m/sec was achieved.

Ignition by spark, pyrotechnic, and explosive, at ambient and 60°C, for liquid without and with bubbles 1 - 3 mm and 4 - 7 mm sizes.

JH: This is a comprehensive study, but not on NM.

28

"Ignition of NOS 365 Liquid Propellant Containing an Air Bubble Under Simulated Breech Pressurization Conditions," Vincent M. Boyle, Edwin A. O'Leary (BRL), Technical Report ARBRL-TR-02236, April 1980.

Pressure generated within a liquid containing a suspended air bubble for volume varied from 1 to 200 microliters. Maximum test pressure was about 600 MPa (6000 atm) and pressurization rates ranged from 2.5 MPa/msec to 800 MPa/ msec. JH: This range would ony be significant for sympathetic detonation, not applicable for adiabatic compression in filling. Uses activator for small scale experiments. Conclusions that bubble sensitizes, larger bubbles more so, and that pressurization rate is important, are well known. JH: Problems that would have to be dealt with if activator were proposed for single bubble in NM studies are outlined. Done with NOS 365, not NM.

"Compression Ignition Sensitivity of Liquid Monopropellants at Temperature Extremes," N. A. Messina, L. S. Ingram, and S. A. Traicarico (PCRL), 25th JANNAF Combustion Meeting, October 1988.

For water-based monopropellants with hydroxyl ammonium nitrate as oxidizer (HAN), a systematic increase in sensitivity to compression ignition is indicated by the results as the conditioning temperature is increased from -40°C to 55°C. Residual ullage and cavitation bubbles influence sensitization to compression ignition. Compression Ignition Sensitivity Tester of PCRL used. The kinematic viscosity of HAN increases by three orders of magnitude over temperature range. **JH: How does NM compare with HAN for which viscosity is O(1) at 65°C and O(1000) cSt at -55°C?** At the low temperature extreme, ullage, bubble size and distribution become critically dependent on injection procedures (as large as 0.1 inch). This could have severe consequences on sensitivity to compression ignition. **JH: Note that the effect of temperature depends on which effects dominate; kinetics, vaporization increase with temperature; viscosity decreases with increase in temperature as does compressibility. Gels are very sensitive to compression ignition. Experiments with NM to determine domains in which particular parameters dominate sensitivity for the TEXS fill procedure and stimulus worst case are essential.** Description of tester used does not correspond to the "water-hammer" effect. However, the approach could be altered to simulate both the loading for TEXS and the stimulus for a worst case.

Data for HAN [**JH: Could be different for NM.**] "clearly demonstrate that the compression sensitivity with embedded air bubbles at -40°C is significantly REDUCED compared to test results at ambient temperatures, up to mean liquid pressurization rates of 690 MPa/sec (10 Kpsi/millisec). (It follows that for HAN at the low temperature extreme, kinetics may have dominated.)

30

"Compression Ignition Hazards of Liquid Monopropellants for Gun Applications," N. A. Messina, L. S. Ingram, and M. Summerfield (PCRL), 20th JANNAF Combustion Meeting, CPIA 383, Vol II, pp 135-160, October 1983.

It has been determined that "water hammer" peaks of approximately 1000 psi and liquid pressurization rates of the order of 10 Kpsi/msec have never resulted in an ignition event during the fill procedure for any of the liquid monopropellants considered (water-based with hydroxyl-ammonium nitrate as oxidizer). **JH: Significance for NM depends on comparison of compressibility, vapor pressure, kinetics, etc., and filling conditions.** Largest bubbles identified in filling procedure were 0.015 inch.

Compression ignition can occur if cavitation associated with rapid-fill is severe enough or if gas ullage is introduced into the system and the compression rate is high enough. A finite induction time related to confinement precedes runaway. **JH: Properties of NM may alter these statements.** The

tendency to achieve a compression ignition event depends on mean pressurization rate, rather than the instantaneous maximum pressurization rate.

31/610

"Compression-Ignition Sensitivity Studies of Liquid Monopropellant in a Dynamic-Loading Environment," N. A. Messina, L. S. Ingram, P. E. Camp, and M. Summerfield (PCRL), 16th JANNAF Combustion Meeting, Monterey, CA, September 10-14, 1979, pp 247-284.

Adds to air bubbles, possibility that bubbles may be "simply vapor-filled, formed by cavitation during the filling process." JH: **High vapor pressure of NM makes this an important consideration, particularly at high temperatures.** Whether detonation occurs depends on the quantity of bubbles acting simultaneously. Describes the flow visualization equipment and studies. Shows differences between water and a liquid propellant (not NM). Describes the compression-ignition sensitivity equipment and studies. Shows need for adequately large bubbles to produce reaction under conditions of pressure profile and collapse rate. For slow kinetics and tiny bubbles, transport prevents runaway reaction or ignition. JH: **Provides the limited experimental data to support the PCRL theoretical treatment of bubble collapse.**

32

"Theory of Bubble Dynamics in Condensed Explosives During Start-Up Transient," M. Ben Reuven and M. Summerfield (PCRL), 17th JANNAF Combustion Meeting, Hampton, VA, September 22-26, 1980, Vol II, pp 259-286.

Provides a critical review of bubble dynamics literature and sets up an analytical model for study of a single bubble in an infinite field which includes: (1) compressible condensed phase, (2) chemical reaction in both condensed and gas phases, (3) non-equilibrium vaporization/condensation at the bubble surface, (4) non-uniform temperature field within the bubble, and (5) time-varying $P_0(t)$. This is based on PCRL-FR-79-004, July 1979. JH: **This paper and PCRL report (33) are definitive theoretical treatment.** Behavior is linked to physical properties, in particular, compressibility of the liquid acting to moderate the energy into the gas bubble. Like a spring-mass system, the bubble undergoes many cycles before the oscillation energy is dissipated by heat transfer and viscosity. Integrated effect can lead to runaway reaction.

JH: **Experimental proof of this theory is limited. See PCRL report cited (33).**

33

"Compression-Ignition Sensitivity Studies of Liquid Propellants for Guns," Neale A. Messina, Larry S. Ingram, Preston E. Camp, Moshe Ben Reuven, and Martin Summerfield, Princeton Combustion Research Laboratories, Inc., Report No. PCRL-FR-79-004, July 1979.

This is a PCRL Final Report on compression-ignition sensitivity studies. From the presented theory and physical properties, stimulus properties, and kinetic properties it is possible to generate a hazard plot showing the regions of benign, reaction, and possibly detonation consequences. The paper (32) at 17th JANNAF Combustion Meeting by M. Ben Reuven and M. Summerfield is more concise and should be read concurrently with this report. More recent papers provide no major changes. **JH: This report was a major expansion of the existing treatment of collapse of gas bubbles. See comments on my summary of JANNAF reference cited.**

34

"Progress Report on a Mechanism for the Compressive Ignition of Liquid Monopropellants," Walter F. Morrison, John D. Knapton (BRL), and John Mandzy (GE), 17th JANNAF Combustion Meeting, Hampton, VA, September 22-26, 1980, Vol II, pp 287-307.

Presents a model of the collapse of a gas bubble in an incompressible liquid and the combustion of the surrounding liquid after ignition occurs. **JH: The PCRL model had a compressible liquid and concluded that compressibility was a critical parameter.** Unless the pressurization of the liquid is very gradual, some asymmetry in the bubble will be generated by the passage of the pressure wave. It has been shown (ref cited) that the surface of a collapsing bubble containing only liquid vapor is unstable and that perturbations of the liquid surface during collaspe can result in breakup of the bubble. Therefore the assumptions of spherical symmetry and stability may not be valid. **JH: This includes the PCRL model. Emphasizes the need for studies with NM under conditions simulating the TEXS problem. Only experiments can handle bubble asymetric collapse.**

35/412/611

"Sensitivity of Liquid Monopropellants to Compression Ignition: A Progress Report," N. A. Messina, L. S. Ingram, and M. Summerfield (PCRL), 19th JANNAF Combustion Meeting, Greenbelt, MD, October 4-7, 1982, Vol I, pp 521-533.

Bubbles may be brought into the chamber during loading or may be formed by cavitation during the filling process. Visualization was done for a piston ram system. The liquid is somewhat compressible, and the compression wave propagates through the column with a finite velocity, stagnating the fluid to meet boundary condition. The pressure pulse collapses cavities producing hot spots. "Water hammer" peaks of 1000 psi and pressurization rates of 10 Kpsi/ msec are obtained. However, for those liquids considered, igni-

tion has not occurred. Propellant was .ot re-used because of bubble content and possible change in rheological properties. Used a compression ignition sensitivity tester to do tests versus bubbles in liquid. Found a finite induction time needed for pressure generation due to gas evolution, and run-away reaction always occurred well afterward. Confinement time under pressure is thus a factor. **JH: Not for NM. Parallel studies for TEXS are needed.**

36/612

"The Role of Physical Properties in Dynamic Loading Processes and Bubble Collapse of Liquid Monopropellants for LPG Application," N. A. Messina, H. H. Tseng, L. S. Ingram, and M. Summerfield (PCRL), 21st JANNAF Combustion Meeting, Laurel, MD, October 1-4, 1984, Vol II, pp 515-527.

The real fluid effects that are important in bubble collapse dynamics are vapor pressure, density, viscosity, surface tension, liquid compressibility. Modifies Rayleigh equation. Finds viscosity reduces rate of bubble collapse. Surface tension effects always acts opposite to gas pressure and vapor pressure effects. Surface tension dominates for small bubbles, but these are not important for ignition by adiabatic compression. Provides methods for measurement of the relevant physical properties.

JH: This is not for NM. A study such as this for NM is required, with real property relevance for TEXS dynamic range and temperatures of military interest used to set domain of interest.

37/334

"Ignition and Pressurization of Bubble Regions in Energetic Liquids," Dennis J. Caldwell (Hercules-Utah), 21st JANNAF Combustion Meeting, Laurel ,MD, October 1-4, 1984, Vol II, pp 501-513.

"Jarring a liquid can first cause cavitation followed by pressure pulses strong enough to ignite the bubbles by compression heating. This aggregate will rapidly pressurize, leading to a strong deflagration or detonation event, depending upon external conditions. When the liquid is inhomogeneous, initiation thresholds can be an order of magnitude lower (than for homogeneous)." Bubbles can focus energy into small regions, which reach higher than average temperatures.

Extends the model of Hay and Watson [6th Detonation Symposium (13)] for a system of burning bubbles in order to incorporate viscosity. **JH: Still saddled with incompressible fluid and linear burn rate.**

"Sensitivity of Liquid Monopropellants to Compression Ignition," N. A. Messina, L. S. Ingram, and M. Summerfield (PCRL), 18th JANNAF Combustion Meeting, Vol II, pp 269-287, 1981.

Identifies the problem as defining the safe domain of operation. Provides information on transport visualization chamber and pneumatic load cylinder. Presents test considerations for determining by compression ignition sensitivity test the threshold conditions for runaway reaction. Summarizes results as a three dimensional plot based on the critical parameters--pressurization rate, volumetric air ullage, or distributed with particular bubble profile and injection pressure.

JH: Although not done for NM, the framework for consideration would be useful for TEXS. However, the domain of parameters is different for TEXS.

39

"Progress Report on Compression Ignition Sensitivity of NOS-365," J. Mandzy and K. Schaefer (GE), J. Knapton and W. Morrison (BRL), Procedings of the 1980 JANNAF Propulsion Meeting, Vol I, pp 377-398, 1979.

"If the breakup of the ullage bubble is rapid compared to the action time of the processes responsible for generating ignition and cooperative effects between bubbles are negligible, then the size of the original bubble is immaterial. What really matters is the size of the bubble when the processes responsible for ignition become appreciable." JH: For NM case this stresses need for bubble profile that exists at time of any compression wave. The ignition threshold depends strongly on pressurization rate which is related to ability of bubble to dissipate the energy and also is related to magnitude of the pressure gradient across the bubble and therefore is a measure of the tendency toward unsymmetric collapse.

40

"Progress Report on Compression Ignition Sensitivity of NOS 365 Under Rapid Propellant Fill Conditions," J. Mandzy and K. Schaefer (GE), J. Knapton and W. Morrison (BRL), 17th JANNAF Combustion Meeting, Vol II, pp 309-327, 1980.

This is a second progress report [the first is (39)] that deals with rapid loading versus slow loading in the first progress report. For rapid loading, the physical state of the propellant is characterized by the presence of turbulence and a finely distributed ullage field. With the ullage dispersed throughout the fluid volume, any given bubble is quite small compared to the fully coalesced case. For the same applied pressure field, it then becomes more difficult to achieve as high a temperature in the gas bubble. The surface to volume ratio of the bubble increases as the bubble radius decreases, favoring heat loss by conduction to the surrounding liquid, making ignition less likely. JH: The higher surface area also makes

"flash" burning possible, particularly in the presence of vapor and oxygen. See WSTF paper on froth (50-53).

41/413

"Dynamic Loading of HAN-Based Liquid Monopropellants at Temperature Extremes," N. A. Messina, L. S. Ingram (PCRL), 24th JANNAF Combustion Meeting, pp 471-483, October 1987.

A transparent chamber is used to evaluate rapid fill (through gun valve) of liquid propellant from ambient down to -55°C, in which range viscosity increases by three orders of magnitude. From 20° to -40°C some ullage is observed. Between -40°C and -55°C change occurs—"discrete bubbles distributed through the liquid at -55°C assume non-spherical shapes; injection times increase by a factor of 3 to 5; large pockets of undivided ullage occur." JH: This is not NM, but it suggests critical viscosity occurs at a temperature, and pumping and bubble characteristics change sharply. Effects for centrifugal pump will be different. Although not done, equipment can do swirl injection.

42/614

"Nitromethane Based Monopropellants," U.S. Air Force Technical Report AFRPL-TR-81-17, 88D176-D183, May 1981.

U-tube adiabatic compression test described. Driving pressure of nitrogen acts on 2 mL of liquid via a rapid opening valve (90% open in 1 msec—for 500 psig rate is 5.2×10^5 psi/sec). Up and down procedure used with positive result, one in which the stainless steel tube is ruptured by explosive decomposition (severed or fragments torn out). Negative: intact or split. For NM Figure 1 gives details of apparatus. Propellant sample is in $\frac{1}{4}$ inch o.d. tube at base of U test section. Approximately 5 $\frac{1}{2}$ inch height (on side away from accumulator) of tube is region in which nitrogen gas is compressed against plug.

Driving Pressure (psig)	750	700	650	600	550	500	450
Pressure Ratio	52.0	48.6	45.2	41.8	38.4	35.0	31.6
Positive Results	2	2	1	1	1	1	0
Negative Results	3	2	2	2	1	2	10

JH: No included bubble. Small diameter, probably no froth. Small surface area of liquid in contact with compressed gas, metal surround. Not clear what is pressure and thermal loading of NM versus time.

43

ANGUS responses to U.S. Army letter dated 17 December 1986 regarding DAAA-21-86-K-0333, Technical Evaluation for TEXS Program.

Question - p 13 - At 125°F, what pressure will cause adiabatic compression of NM without a nitrogen blanket? Response - Adiabatic compression refers to vapor phase. Rate of compression, heat transport away, are important. Ignition of NM vapors will occur above 785°F. Pressure must be maintained for deflagration of liquid to follow and run-up to detonation to occur. Drum rupture asserted to precede monopropellant burning. Cites Bellinger (58). Autoignition of liquid NM does not occur with pressures up to 90,000 psi. Cites Anderson (330). States presence of nitrogen blanket or absence of no consequence.

JH: Does not account for vapor presence of NM versus temperature of liquid. If splashing, setback, etc., occur, thin films in contact with nitrogen (versus air) may be less ignitable.

Question - p 15 - Discuss the filling process with respect to the prevention of introducing air into the pumps/pipeline during pump out of air. Response - "A centrifugal pump cannot force liquid through a full discharge time when operating on air because the pressure developed with air is significantly less than the liquid developed pressure." Did experiment (described) with transparent hose to verify this. Air due to empty hoses at start purged with float principle automatic air vent. **JH: Demonstration under field conditions of full sequence required.**

44/405/502

Technical Data Sheet, ANGUS Series TDS No. 2, 4th Edition, pp 7-8.

"The pressure of confined liquid nitromethane increases 17.5 atm for every 1°C increase of its temperature. Any pockets of vapor or gas will slow the pressure rise, but small pockets can be compressed rapidly enough to heat the gas and even to ignite the nitromethane." Adiabatic compression can occur in a pipe in which the flow of liquid is impeded so that most of the kinetic energy of the moving liquid is expended in compressing a pocket of gas. "Higher pressures without explosions can be tolerated by NM in contact with nitrogen—because it cannot induce ignition and support combustion." Experiments with oxygen showed explosions with reservoir pressures as low as 250 psi, with nitrogen required 850 psi minimum. In thick-walled containers, believe 0.50 caliber high velocity bullet transfers energy to compress gas in head space causing observed explosion, but needs vapor space for explosion. For thin-wall container, explosion does not occur. Pressures necessary for monopropellant burning exceed rupture value for 55 gallon DOT 17E steel drums. "Handling systems should be designed so that pressures cannot exceed 100 psig, even with improper operation. If higher pressures are necessary, extra precautions must be taken to prevent occurrence of adiabatic compression."

Exposure of rats to NM vapor - 13,000 ppm (33 g/m^3) in air, 6 hr - death

2,500 ppm (6.3 g/m^3 in air, 4-6 hr in 4 days, died fifth day.

745 ppm - 8 wk decrease in rate of body weight gain - 1 month some pulmonary abnormalities.

"Standard of 100 ppm for NM was judged to provide a satsifactory margin of safety for workers exposed to its vapors."

American Conference of Government Industrial Hygienists have set 100 ppm (~ 250 mg/m^3) as threshold limit value for an 8 hour-per-day working exposure. This time weighed average accepted by OSHA.

If prolonged exposure to NM vapors above threshold occurs, need a mask supplying fresh air or self-contained breathing apparatus. Such exposure may occur "as a result of spillage." "ORGANIC-VAPOR CANISTER GAS MASKS SHOULD NEVER BE USED FOR PROTECTION FROM NM VAPORS." JH: **Such gas masks introduce a new severe hazard.**

JH: Calculation of vapor concentration due to vapor pressure in a confined space as a function of temperature of liquid should be done. Leak/opening drum? Measurement of vapor concentration over full field sequence required to compare with threshold.

45/615

Nitromethane TEXS System, Safety Assessment Report (SAR), June 1988, ANGUS Chemical Company.

Appendix B quotes (42) and (614) giving test design for U-tube adiabatic compression test with results—includes ether tests. Appendix C responds to question of hazard of self detonation during pumping—has analysis. Pages 14 and 15 of separate safety assessment report discusses in 4.3 sensitivity to adiabatic compression.

Appendix B gives results for NM and details of U-tube apparatus taken from AFRPL-TR-81-17 dated May 1981. [See summary of (42).] Also had liquid drop weight tests (ASTM-D-2540) and thermal stability test (Liquid Propellant Test Methods, Test No. 6). With a 4 kg weight disc, rupture occurs with water at 190.7 (50%) kg-cm and for NM > 160 kg-cm, i.e., greater than 80% of water value. Reference n-propylnitrate burst disc using a 2 kg weight of 7 kg-cm. Therefore, NM liquid insensitive. Thermal stability test shows major exotherm at 570°F and burst disc rupture which requires 5300 psi at 685°F.

Appendix C gives math analysis for converting the flow energy to potential energy in the form of a compressed elastic medium in a completely rigid pipe with the piston coming to a complete sudden halt (no bounce). Finds must exceed 785°F for 100 microseconds to have potential for self detonation. Then does water hammer calculation for 4 x 25 gal/min of 8.5 psi as initial

45

flow. Gets 100 psia and T = 428°F which does not meet minimum for detonation. JH: See (408).

JH: This calculation ignores bubbles and froth consistent with ANGUS position that no air enters. An error regarding air adiabatically compressed above that threshold could be catastrophic.

46

Reserved for future use.

47/751

"Recent Developments in Nitromethane Based Explosives," Richard S. Egly (Comm Solv), Proceedings of the Symposium of Military Applications of Commercial Explosives, Defense Research Establishment, Valcartier, Quebec, Canada, pp 190-218, PA U-148-396, November 1972.

This is a survey paper. Table 2 has physical and thermodynamic properties. Two hazards: (1) nearby explosion and (2) confined burning of NM. The viscosity and surface properties of NM are such that even quite small gas bubbles will rise rapidly to the surface and break." Bubbles do coalesce. The preferred entrapping materials are small thin-walled, hollow gas filled bubbles--1.5% of microballoons suffices to make NM sensitive to a No. 8 cap and 2.5% to a No. 6 cap.

Freezing point given as -28.55°C or -19.4°F. Gives data on use of methylene chloride in NM as a freezing point depressant (p 204). 70/30 NM/NC has -40.8°C as freezing point. JH: Supercooling must be considered.

48

"Analysis of Nitromethane Incidents," Richard S. Egly (Comm Solv), Niagara Falls, 22 January 1958. (Includes Mount Pulaski tank car accident.)

There was 76,000 pounds in the tank car, which had been cleaned and filled with good quality NM. It was hit by another car during switching and it was unlikely that it was moving more than 6 mph. Attributes NM tank car explosion as secondary with several choices for the primary explosion such as natural gas, another tank car etc.

Niagara Falls tank car had 8,000 gallons. Mt. Pulaski had 10,000 gallons. Attributes NM tank car explosion at Mt. Pulaski as also secondary with primary explosion another tank car with ammonia residue.

Truck-train collision demonstrated that drums on truck, "though subjected to some pretty severe mechanical shock, pressure, and temperature, the NM was apparently unchanged."

In a 1971 industrial accident involving NM "agreed that liquid expansion had compressed a pocket of air in the top of the pipe, and as pressures increased and the air bubble got smaller, the rate of temperature increase undoubtedly accelerated." Led to explosion, not detonation.

JH: **Need exists to calculate expansion with temperature of NM and pressures developed above liquid.**

49

"Explosives for Tank Traps," Edward James, Angus Chemical Co., Internal Communication.

Survey NM regarding TEXS application considering performance and hazards. Failure diameters: in glass - 12°C, 20 cm; at 24°C, 36 cm; in brass tube 2.9 cm. "It is not primarily the gamma of the gas in the bubble, but the hydrodynamic discontinuity that causes the local temperature rise." JH: **Applies to shock initiation, but bubble compression itself is another ignition mechanism that must be considered.**

Arrhenius for p 1, 10, 50 Kbars has pre-factor (log) 40, 5.3, 6 and actuation E 127, 20, 22 Kcal/mol. Heating NM in rigid container from 50°F to 165°F would produce 13,024 psi which would require 302°C for runaway. JH: **Again ignoring energy concentrators, bubble, flow stagnation, crack in drum.**

50

"Hydrazine Rapid Compression Testing," Chemical Propulsion Information Agency Bulletin, Vol 14, No. 5, September 1988.

When a moving column of hydrazine in an inert gas ullage is stopped rapidly, an explosive event occurs due to hydrodynamic surge pressures (water hammer) generated at the dead head. "Photographs of the compression process showed that a froth formed at the liquid hydrazine-gaseous nitrogen interface as the liquid travelled through the gas ullage. It is believed that compression of the froth at the dead head produces adiabatic heating and thermal runaway . . ." JH: **Under similar circumstances, if such occurs in TEXS, this would be a serious hazard. Note that a difference could be expected for air ullage versus nitrogen ullage, and this difference could possibly justify the nitrogen used above the NM in the drums.** References are given to work on the "froth mechanism." (51)(52)(53)

51

Reserved for report/paper in preparation by F. Benz, WSTF, with information on frothing of liquids during flow (see 50).

"Explosive Decomposition of Hydrazine by Rapid Compression of Gas Ullages,"
D. Baker, et al., 1988 JANNAF Safety and Environmental Protection Subcommit-
tee Meeting, Chemical Propulsion Information Agency, May 1988.

Water hammer pressures (hydrodynamic surge pressures) are much greater
than the push pressures accelerating the liquid. For example, a surge pres-
sure of 3600 psi resulted for water accelerated with a push pressure of 200
psi into a line pressurized with nitrogen at 0.1 psia. **JH: For TEXS, push
pressure corresponds to pump action; surge corresponds to pressure when fluid
is dead-headed (stagnated).** Experiments were done for hydrazine, acceler-
ated, and rapidly brought to rest and compared with results for water. Test
system described. As surge pressure increased, a condition was reached where
significant decomposition occurred, raising the pressure above that for
water. **JH: Ullage pressures could exist in drums at higher temperature due
to NM expansion and vaporization.** Ullage gas necessary to initiate decompos-
ition. However, as the pressure of the ullage gas increased, the hydrody-
namic surge pressure decreased and eventually reached a level at which hydra-
zine decomposition could not be initiated. **JH: Gas at higher pressures
acts as a cushion in bringing the liquid to rest, so that lesser pressures
are generated in the rearward compression wave in the liquid.**

Tests were performed in which an 8 inch column of liquid was acceler-
ated by a 500 psi push pressure into a 15 inch long glass chamber pressur-
ized with nitrogen at 12.4 psi. A video camera showed leading region of
cloudiness believed to be a froth created by Taylor instabilities at the
liquid-gas interface, resulting in Helmholtz mixing of gas and liquid (gives
ref.). After impact at the dead head, the froth was compressed by the
liquid column. Froth maximizes surface, and under compression heat transfer
is very rapid leading to rapid thermal runaway. Container rupture occurred
for hydrazine, not for water.

Has excellent review for hydrazine with references, some of which may
be extrapolatable to NM.

53/336/641

"Investigation of Detonations in Liquid Hydrazines," H. Beeson and M.
Plaster, 1988 JANNAF Safety and Environmental Protection Subcommittee
Meeting, Chemical Propulsion Information Agency, May 1988.

Provides a background with references on shock initiation of detona-
tion, low velocity detonation and the role of "hot spots" or energy intensi-
fiers in these processes. Quotes Watson that LVD requires higher sound velo-
city in container than in liquid and wall thickness above a minimum value.
Describes a modified card-gap apparatus with a 2 inch diameter.

Hydrazine did not detonate with a donor charge of 0.49 lb of C-4.
Damage consistent with an LVD in 0.5 inch tubes with 0.035 inch wall thick-

ness was not observed (latter is below the 0.06 Watson criterion) was not observed.

Experimental results indicate that the explosive events observed in rapid compression experiments by Baker (52) involve more complex phenomena than simple shock initiations. **JH: Baker stresses froth compression as key mechanism and considers physical kinetics of froth as control mechanism.**

54

"Calculation of Compression Ignition of Explosives," H. J. Pasman, Symposium on Chemical Problems Connected with the Stability of Explosives, Ystad, May 28-30, 1973 (3rd Proceedings), pp 180-197. (English) CA. 82, 127153a, 1975

Calcn. of explosion iniation by compression of an air-filled cavity in an explosive substance is dealt with. The compression is not caused by shock, but by a relatively slow process, e.g., when a container of the explosive is launched or decelerates on impact. Compression ignition can also be considered as a process of external generation of heat on collapse of a gas-filled cavity and transfer of this heat to the explosive. The process is important to safety; because of the easy formation of gas bubbles, it is of special interest for liquid explosives. Based on a model consisting of a flat, air-filled cavity between a piston and a cylindrical explosive body, an equation is derived based on the theory that ignition starts when the rate of heat evolution from chem. decompn. becomes equal to the rate of heat transfer from the outer source. A series of calcns. were performed with composition B (60% RDX -40% TNT). Results are given for such parameters as air temp., temp. of the explosive surface, air pressure and cavity height versus time, and force of the piston on the explosive surface.

JH: The parameters considered do not list rate dependence of the force of the piston, but the competition between evolution and transport are both rate dependent factors linked to the stimulus rate. Calculations were performed with COMP B, but not with liquid explosives. For the latter, the mechanical properties of the liquid, e.g., compressibility, becomes important.

55/352/642

"Sensitivity of Nitromethane for Low Velocity Detonation," R. R. Ljsselstein (Neth), Propellants, Explosives, Pyrotechnics, 10, 1, pp 14-17, February 1985.

Maps the shock loading regime in which a stable LVD can develop using a modified gap test (details given). Including LVD's, NM appears to have a sensitivity comparable to that of relatively sensitive high explosives. Explanation is that of Watson, with cavitation precursor. Threshold for heavily confined NM with a hollow axial tube for LVD is 1.5 GPa, HVD is 7 GPa (15 Kbars, 15,000 atm). The threshold and violence of an LVD explosion

are strongly influenced by the dimensions, materials of the confinements, and presence of axial inclusions. ". . . under confined circumstances such as may occur for instance when it is pumped through pipelines nitromethane should be treated as a reasonably sensitive high explosive." **JH: The data in this paper are not for the conditions encountered in pumping through pipelines. The threshold for LVD far exceeds any water-hammer generated pressure. It may have value for fragment/plate impact or sympathetic detonation and for propagation of LVD instead of HVD regarding performance.**

Found the distance required to establish an LVD for the strong confinement used here (steel tube i.d. = 31.5 mm, o.d. = 63.5 mm) was 150 to 250 mm which means that test set-up requires a very long tube. (NOL large scale gap test is only 140 mm) or erroneous results may be inferred. The shock velocity of the stimulus may decrease to the sound velocity level before building up to the LVD value (1200 m/s).)

JH: The possibility that the initiation scheme in TEXS will produce LVD instead of HVD, greatly impairing performance, requires serious consideration.

56/351/643

"On the Low-Velocity Detonation of Nitromethane," A. A. Schilperoord (Netherlands), Seventh Symposium (International) on Detonation, pp 575-582, 1981.

Experimental work is described which shows that nitromethane is able to undergo a low-velocity detonation (LVD) reaction, if confined in a steel tube and subjected to a shock wave of appropriate strength. It is concluded that the occurrence of LVD in nitromethane requires such conditions as to enable both cavitation of liquid and sufficient explosive reaction. The latter condition means a rather strong confinement, because of the relatively low reaction rate of nitromethane. The results of this work may lead to an improved design of a gap test for the investigation of the shock wave sensitivity of liquids.

A stable LVD is characterized by a constant velocity higher than the sound velocity of the cavitated liquid.

Results explained by Watson theory. For NM, when sufficient confinement is available, its sensitivity is comparable to that of sensitive high explosives (~ 10 Kbars). **JH: Data is needed for the TEXS configuration; pipe not enclosed and also buried; and versus temperature.**

Dimensions of Steel Tubes with Identification (in mm)

Inner diameter	30	31	31	50	31.5
Outer diameter	35	38	51	70	63.5
Wall thickness	2.5	3.5	10	10	16
Length	750	750	750	750	750
Identification	30/35	31/38	31/51	50/70	31.5/63.5

LVD in 31.5/63 steel tube; marginal in 50/70 and 31/51 which have same wall thickness.

57/617

"Compression Ignition Studies of a Liquid Monopropellant," A. H. Mitchell and H. A. Kirshner, AJAA Journal, 1, 9, pp 2083-2087, September 1968.

Equipment provided control of compression rate, piston travel, velocity, and bounce. Pressure in liquid measured, and high speed photography included. Figures and description given. Piston velocities 5.7, 13.4, 17.3 fps showed more liquid agitation at 17.3 than the lower rates. Measured deviation from pressure for adiabatic compression. Decrease in pressure increased with higher compression ratios attributed to increased cooling of the compressed gas phase with increasing compression ratio due to higher temperature gradients at the turbulent vapor-liquid interface. **JH: Shows need to consider the interface between liquid and gas/vapor in a rapid compression.** Studied ethyl and n-propyl nitrate, not NM. Horizontal compressions appear to give ignition at lower compression ratios for high piston velocities. (Compression ratios > 100:1, 100:1, 80:1, 80:1 for 5.7 13.4, 17.3 fps.) Ignitions at high piston velocities were more violent as a result of the extensive liquid-gas interface obtained. **JH: This is early indication of role of froth. [See (50)-(53).]**

58/414

"Stability of Nitromethane," F. Bellinger, H. B. Friedman, W. H. Bauer, J. W. Eastes, W. C. Bull (Edgewood), Industrial Engineering Chemistry, 40, pp 1320-1324, 1948.

Application of interest transferred 20 gallons of liquid to a chamber in 0.75 second or less. Studies three NM's: (1) 96% NM, remainder mostly nitropropane, small amounts of nitroethane, acetic acid, and water; (2) 96% NM balance as (1); (3) NM purified by fractionation. Dropped 200 gram hammer in ten tests, and assigned 0.1 for detonation, 0.05 for partial detonation, zero if none.

Drop Height (cm)	20	30	40	50
NM (1)	0.00	0.10	0.50	0.65
(2)	0.05	0.40	0.60	
(3)	0.20	0.45	0.90	
Nitroglycerin	0.70			

Shorter hammer fall means NM detonates more easily. Note that pure NM (3) is more sensitive.

It was found that NM would detonate more easily when at atmosphere of oxygen instead of air-filled space. Also, a harder hammer blow was required to cause detonation of NM when the space was filled with nitrogen instead of

air or oxygen. JH: Here again is basis for nitrogen ullage reinforced by possibility of froth mechanism. See (50)-(53) and (57). The sudden application of 2000 psi high pressure gas on NM is likely to cause a detonation even though the NM is free to flow. The use of 1230 psi air pressure under the same conditions appears to be safe. If NM is forced into a closed pipe by 850 psi pressure, it will detonate even if nitrogen is used on both sides of the liquid column. Did tests with 0.50 caliber machine gun at 100 yards, except 200 yards for full 55 gallon drains. NM in 0.25-inch steel wall containers will not be detonated unless 2% catalyst is present. Incendiary ammunition causes explosions and fires even in thin-walled containers. JH: If incendiary ammunition is part of the threat, this is most serious. An empty NM drum (one still containing NM vapor) will explode when hit by incendiary ammunition. NM is relatively inert to tracer fire. Table VII gives full results.

Samples (1) and (2) stored at 50°C in closed container created a partial pressure due to absorption from the air above NM; judged as due to impurities. The samples of NM that resulted from the 50°C storage tests were more sensitive to detonation by impact than the original material. Addition of small quantities of gasoline is proposed as a practical means to decrease the sensitivity of NM to detonation. JH: It is important to test properties at temperature extremes and also after storage periods at temperature extremes. Note that work was done at Guggenheim Aeronautics Laboratory of California Institute of Technology (GALCIT). See (59),(60), and references cited.

60

"Thermal and Shock Sensitivity of Nitromethane," N. Kaplan, S. A. Johnston, R. C. Sill, and L. H. Publes, Jet Propulsion Laboratory, Galcit Progress Report 1-35, December 26, 1945, (U38806).

"It has been found that the sudden compression of air or oxygen in contact with nitromethane can result in an explosive reaction, presumably because of the rise in temperature of the gas by adiabatic compression. Under identical conditions, the compression of nitrogen caused no observable reaction with nitromethane.

Thermal (slow heating) sensitivity of NM was determined in the presence of air or nitrogen above NM. NM will frequently explode at temperatures ranging from 550 to 650°F with either air or nitrogen above the liquid.

Vapor pressure of commercial NM was measured from 70 to 520°F. (See Table 1.)

Results and experimental techniques are described for all above. Data given for decomposition in contact with metals. (See Table 2.)

Table 1. Vapor Pressure of NM

Temp °F	70	100	130	160	190	220	250	280
Pressure psia	0.696	1.52	3.04	5.72	10.1	17.0	27.4	42.3

Temp °F	310	340	370	400	43C	460	490	520
Pressure psia	63.2	91.5	129	178	239	315	409	521

Table 2. Behavior of NM in Contact with Various Materials

Metal Present	Temp °F	Rate of Pressure Increase $(lb/in.^2 \ sec)$	Apparent Decomposition Rate $(ft^3 \ gas \ stp/ft^3 \ liq \ sec) \times 10^4$
None	405	0.016	1.8
	465	0.06	2.6
	505	0.12	6.4
	544	0.23	8.1
Stainless	304	0.003	0.2
Steel AISI 303	464	0.15	7.5
	505	0.15	9.2
	545	0.38	14.0
Mild Steel	505	0.10	6.0
1020	545	0.18	5.2
Aluminum	504	0.12	4.1
Alloy 356	545	0.18	8.5
Copper	504	0.19	13.0
	544	0.26	12.0

61

"Ignition of Normal Propyl Nitrate by Compression of Air-Normal Propyl Nitrate Vapor Mixtures," E. A. Hogge and J. B. Levy, NAVORD Report 4296, May 1956. (AD 98362)

Report only on NPN vapor-air mixture above liquid NPN subjected to rapid compression using a locked stroke compressor (references given). Peak pressures in the range of 700 - 800 psia with compression times of 1 - 4

msec were obtained. The bubble was compressed until it became hot enough to ignite. The vapor then burned out. In the larger bubbles this occurred early, at about ½ final pressure; for smaller bubbles, near final pressure. The failure of burning to propagate through liquid attributed to pressure generated in bubble being too low due to vapor burn. Gives calculations to explain results. Analysis permits predicting ignition temperature for NPN-air bubbles corresponding to a 13:1 compression ratio in perfect adiabatic compression. JH: **Idealized equipment and analysis compared to TEXS and not for NM. Does, however, suggest an approach for getting NM data of ignition versus compression ratio and rate of initial conditions.**

62

"Fundamentals of Liquid Propellant Sensitivity," T. A. Erikson and A. J. Tulis, AFRPL-TR-67-81, March 1967. (AD 827962)

The sum total of shock-tube testing experience is the recognition that there is an involvement of vapor supply mechanisms as well as chemical reaction mechanisms at an interface. The combination governs ignition and growth. For explosive response, it is found that disruption or particulate forms on the surface. JH: **An indication of the froth mechanism.** The focal point of explosive sensitivity appears to rest in hot gas-surface energy interchange; e.g., bubble compression, film boiling, energy transfer to condensed phase. "In any situation in which the vapor supply is free, there is little endothermicity to inhibit the runaway of potential chemical reactions. JH: **NM has a high vapor pressure. Nitrogen mixed with vapor helps retard chemical runaway.** Vaporization rates depend on the surface temperature and the external gas pressure. JH: **Hence vapor role will be greatest at high temperature end of range. For numerical values versus temperature and pressure are needed to do adiabatic compression calculations.**

63

"The Ignition of Liquid Monopropellants by Acoustic Cavitation," M. S Campagna, U. S. Naval Academy, U.S.N.A.-T.S.P.R. No. 65, 1975. (AD A015953)

Experimentally determined the minimum value of energy density necessary to initiate a chemical reaction as 2.5 joules/cm^3/sec. Suggested an acoustic cavitation ignition scheme. Quotes two models—a bubble which oscillates nonlinearly about an equilibrium radius and a collapse per Rayleigh description until internal pressure stops inward motion. The cavity pressure depends on amounts of vapor and gas. JH: **It is well recognized that this is an oversimplification. All the parameters must be delineated and included. Some dominate according to the situation.**

64

"Initiation and Decomposition of Nitromethane at 10 Kbar Pressure (Ignition and Non-Detonating Decomposition of Liquid NM Explosive at 10 Kbar Pressure)," S. P. Gill (PI), Astronautica Acta, 15, pp 427-438, International Colloquium on Gas Dynamics of Explosives, 2nd, Novosibiorsk, August 24-29, 1969.

Initiation phenomena cannot be explained on the basis of an Arrhenius reaction rate in homogeneous NM because there is a difference by a factor of 10^{11} between observed and calculated induction times. Initiation by adiabatic compression of air bubbles is the most likely explanation. Derives a theoretical expression for induction time for heating by compressed air bubbles by using real gas equation of state, laminar heat conduction at gas-liquid interface, and an Arrhenius reaction rate in decomposing NM with favorable but not conclusive results. See (33) for more sophisticated treatment of bubble collapse initiation.

65

"The Pyrolysis of Nitromethane Part 3 Simulation of a Simplified Mechanism," A. Perche and Michel Lucquin (France), J Chem Res (S), pp 306-307, 1979 and J Chem Res (M), pp 3527-3285, 1979.

For isothermal pyrolysis between 400 and 500°C a simulation of species evolution versus time is plotted in Figure 1 (with rate constants of 26 involved reactions in Table 1) and compared with experiment. The principal species NO, H_2O, $\frac{1}{2} \times \Delta(CH_3NO_2)$, CO, CH_4 track very well; the others are correct as to order but vary in slope. Then using the technique, a non-isothermal simulation is done which correctly coincides with experiment for predicting explosion limits for the range 455 to 500°C. JH: **This paper shows the complexity of NM decomposition. To include chemical decomposition in a full theory of bubble collapse would require either use of all these reactions (in a subprogram) or some approximation, possibly based on the overall energy release rate which underlies the explosion limits.**

66

"Investigation of the Thermal Initiation of Detonation in Nitromethane," R. H. Guirguis, JAYCOR, Alexandria, VA, J206-83-011/6223, Order No. AD 136 211, p 32, 1983.

From Chem Abstracts, Vol 101, 1984, 101:75222j:

Shock-tube expts. and extensive numerical simulations were used to provide information required to construct a detailed chem. mechanism for the decompn. of gaseous nitromethane diluted in Argon. Measurements were made of the time evolution of the pressure and the NO adsorption at a fixed location in the shock tube, and mass and IR spectroscopy were used to identify the products. Expts. were performed at 0.3-2.5 atm and 700-2000 K using mixts.

of 10-100% nitromethane in Ar. A mechanism composed of elementary reactions describing nitromethane decompn. in the range of the expts. was compiled, tested, and reduced to a set of 62 most significant reactions. See (65) for reactions. See (67), (68) by same author.

67

"Chemical Studies of Nitromethane - A Prototype Energetic Material," R. Guirguis, D. Bogan, D. Hsu, and E. Oran (NRL), Conf: Chemical and Physical Processes in Combustion, 1982 Fall Technical Meeting, Eastern Section of the Combustion Institute at Atlantic City, NJ, December 14-16, 1982. E.I. Conference No. 02306, J1 Announcement 8308.

JH: A complete treatment of adiabatic compression must include the NM vapor and the contribution by reaction of this vapor as ignition and growth occur. To do this the chemical pathway and kinetics are needed for the range of temperatures and pressures of interest. NRL made meaurements, but results were given orally, not printed here.

"Early shock tube studies have reported two hypotheses for the first stage in decomposition: simple band rupture to give CH_3 and NO_2; and unimolecular rearrangement to methyl nitrate followed by band rupture to give CH_3 and NO." The range of pressures and temperatures by A. Perche and Michel Lucquin, J. Chem Res, 306, 1979 (65), see (68), (<800 K) not of interest to these authors. **JH: But, this range may be of interest regarding TEXS as it determines possible ignition early on.**

68

"A Mechanism for Ignition of High Temperature Gaseous Nitromethane - The Key Role of the Nitro Group in Chemical Explosives," R. Guirguis (Berkeley Research) and D. Hsu, D. Bogan, and E. Oran (NRL), Combustion and Flame, 61: 51-62, 1985.

A detailed chemical mechanism describing ignition of high-temperature pure gaseous nitromethane was compiled and tested using shock tube experiments. The temperatures and pressures behind the reflected shock were in the range 1000-1600 K and 1-10 atm. Measurements were made of the time evolution of the pressure at the end wall, as well as of the simultaneous pressure and NO absorption at a short, fixed distance from the end wall. Mass and infrared spectroscopy were used to identify the final products. In the reaction mechanism proposed, initiation starts with the C-N bond breaking which yields CH_3 and NO_2. Methoxy and CH_2NO_2 radicals then propagate the reaction through two major parallel pathways, both producing CH_2O. Formaldehyde is then reduced to HCO and carries the reaction toward completion. The radical reactions do not release enough energy to compensate for the energy consumed in breaking the C-', bond. Although most of the radicals reach their maximum concentration early in the reaction process, ignition does not occur until virtually all of the nitromethane is consumed. The calculations show that the nitro group is the key to explosion: NO_2 produces OH through

its reaction with H radicals. Hydroxyl reactions, which are fast and exothermic, lead to an accelerated consumption of the explosive with heat release. Comparison with the experiments shows that the mechanism predicts correct induction times for the pressure and temperature range of the experiments.

JH: Note particularly that 1000-1600 K and 1-10 atmospheres are in a range of interest for TEXS. Reaction rate constants are given in Table 1 for all above. Induction times for NM are of the order of 25 microseconds for the range and are given in Table 2. No ignition occurs for 4 atm and ~1000 K. **JH: This paper provides chemical kinetics relevant to TEXS computer model.**

69

"Effects of Pressure on the Thermal Decomposition and Chemical Reactivity of HMX, RDX, and Nitromethane," G. J. Piermarini and S. Block (NBS) and P. J. Miller (NSWC), Combustion and Detonation Phenomena, pp 15-1 through 11, 19th International Conference, June 29 - July 1, 1988, Karlsruhe, Germany.

Diamond anvil cell used to study decomposition of NM to pressures are as high as 7.1 GPa (71 Kbars) and temperatures up to 583 K. For NM, the rate increase with increasing pressure indicated an overall bimolecular-type rate reaction. "The decomposition of NM appears to be complex and varies over large changes in pressure." Above 1.54 Gpa and 433 K, thermal decomposition initiates. Single crystals grown from the liquid, if pressed rapidly above 3 GPa, explode by stress created within. **JH: Does this lend to any extrapolation to the sensitivity of frozen NM which would also be crystalline?** Two decomposition mechanisms exist, one dominating below 4 GPa and T $\leq$ 130°C, the other above—they have different time dependencies. Above 5 GPa, a third mechanism dominates. Gives proposed mechanisms based on electronic orbital calculations. Raises question about role of aci form. See (70).

70

"Production of the Nitromethane Aci Ion by Static High Pressure," Roy Engelke, David Schiferl, C. B. Storm, and William L. Earl (LANL), J. Phys Chem, 92, pp 6815-6819, 1988.

Reviews literature on role of aci-ion/form on NM decomposition with reference citation. Presents experimental evidence that static high pressure ~2 GPa (20 Kbar) produces an increased concentration of $(CH_2NO_2)^-$, the aci ion of NM. This results in a self-explosion sensitization. Nitronic acid, the aci form (CH_2NO_2H), is not the causative agent for the sensitizations studied.

The time required to produce the complete exothermic chemistry in steady NM detonation is ≈10 nanoseconds. JH: For homogeneous pure NM, the detonation zone at 6320 m/sec is ≈6320 x 10^{-8} m or 0.632 mm or 63 microns for high velocity detonation, but considerably longer for LVD. Value seems too short.

JH: For TEXS, primary interest is in initation by adiabatic compression and LVD (low velocity detonation). For these, the physical mechanisms of bubble collapse are critical, with the chemistry important, but not necessarily the same as for HVD. Here we have static pressures of 20 Kbars for aci significance. See also (71) regarding alternate decomposition mechanism.

71

"Chemical Sensitization of Nitro Compounds," M. D. Cook and P. J. Haskins (RARDE), Combustion and Detonation Phenomena, pp 85-1 through 8, 19th International Conference, June 29 - July 1, 1988, Karlsruhe, Germany.

Pure NM is very insensitive—in gap test found 13 mm of perspex (Lucite) as the threshold. With DETA (amine), addition, NM becomes very sensitive. Failure diameter decrease of 43% occurs for one molecule to 5500 of NM. Discusses other sensitizers. Investigated sensitization of other nitroalkanes-nitroethane, 2-nitropropane, 2 methyl-2-nitropropane by amines and found all pure forms to be insensitive. Interprets results in terms of ab-initio molecular orbital calculations.

Concludes, "The results of our experiments do not appear to be consistent with the hypothesis that the sensitization of nitro compounds is due to an increase in the concentration of aci ions." See also (70).

JH: A few papers have been included on decomposition and sensitization of NM to provide a possible starting point if future directions should require this. For TEXS this subject is of current secondary interest.

72

"Effects of Thermal Conduction in Sonoluminescence," Robert Hickling (Cal Tech), J. Acoustical Soc Am, 35 (7), pp 967-974, 1963. For more detail, see Cal Tech Rpt, AD 291 647, 1962.

The advance of the collapse generates pressure in the bubble so that contained gas becomes momentarily (weakly) incandescent. It appears to resemble a black body radiating between 6000 K and 11,000 K. For very small bubbles, less than 10^{-3} cm, heat conduction to the liquid is appreciable so the process is not adiabatic. Heat loss reduces temperature within the bubble, affecting radiation. In Table 1 below, one sees that radiation intensity varies inversely with thermal conductivity of gas (in water). "Although the thermal conductivity of the liquid is generally about ten times greater than that of the gas, the thermal diffusivity of the gas will still be much greater than that of the liquid. Hence the thermal effects due to a trans-

fer of heat out of the cavity will be confined to a comparatively narrow region of liquid next to the interface. Since the temperature gradient in the liquid has its greatest value at the interface, and since it will be about ten times smaller than the gradient in the gas, it follows that the temperature rise at the interface is small in comparison to the temperature rise in the interior of the gas." Does analysis related to this point.

	Relative Intensity	Thermal conductivity cal/cm/sec/°C x 10^3
Helium	1	0.3365
Neon	18	0.1092
Argon	54	0.0385
Krypton	180	0.0212
Xenon	540	0.0124
Hydrogen	–	0.414
Oxygen	35	0.0583
Nitrogen	45	0.055

JH: The case considered here is NOT the case for NM in the TEXS program. It is important to read this paper and do an analagous consideration for the latter. He assumes a spherical cavity in an incompressible liquid containing an ideal gas with negligible quantities of the liquid vapor; that both gas and liquid are non-viscous; and that temperature rise in liquid in contact with gas is negligible by quote above. For TEXS, bubbles can be larger due to inclusion in pumping or motion; NM is compressible and viscous (at low temperatures); and NM has a high vapor pressure (at high temperature). Thermal diffusivity and surface area change during collapse as shape, pressure and temperature change and turbulent effects occur. To consider the TEXS case, several models for high and low and normal temperatures at start for different bubble sizes need to be considered using the most comprehensive model available. (See PCRL work as possibility.)

73

"Initiation of Nitroglycerin," C. H. Winning (duPont), Explosivstoffe, No. 2, pp 34-38, 1963.

"It appeared that luminous, high velocity detonation started in the cavitated zone between the cap and the corner of the cell, presumably because the expanding gas globe from the cap adiabatically compressed and collapsed the numerous small cavitation bubbles. A deflagration to detonation process ensued." In tubes, detonation propagated as a consequence of cavitation following the reflection of a rarefaction from the exterior of the plastic tube. JH: This paper shows photographic evidence to support surveying the TEXS configuration not only for added bubbles and compression waves, but also for possible release surface that could lead to cavitation.

"Compression Sensitivity of Monopropellants," G. A. Mead, ARS Journal, pp 192-198, March 1959.

In equipment described, a gas bubble in contact with liquid is subjected to rapid compression by a gas driven piston. Rates of pressurization can be adjusted. Sample chamber volume is about 2.3 mL. Samples from about 0.4 to 1.1 mL liquid volume and from 0.2 to 0.9 mL bubble volume can be tested. Preheating or cooling is possible. Analysis of tester action is provided.

NM was tested in the presence of 0.2, 0.4, and 0.8 mL air bubbles. A positive result represented essentially complete decomposition; negative unaffected. Sensitivity of NM was 10.4 ± 1.7 kg-cm/mL. Figure 10 with data is below.

JH: **Here the piston represents the inertia of a liquid column and the pressure pulse generated depends on the time interval in which the pressure peaks. It does not appear possible to extrapolate from this data to the water-hammer ignition of NM.** Note that sensitivities are given for other liquids—in particular n-propyl nitrate is 6.7 ± 2, and hydrazine is >144; i.e., NM is at least one order more sensitive than hydrazine and about the same as n-propyl nitrate. JH: **Significant regarding other studies.**
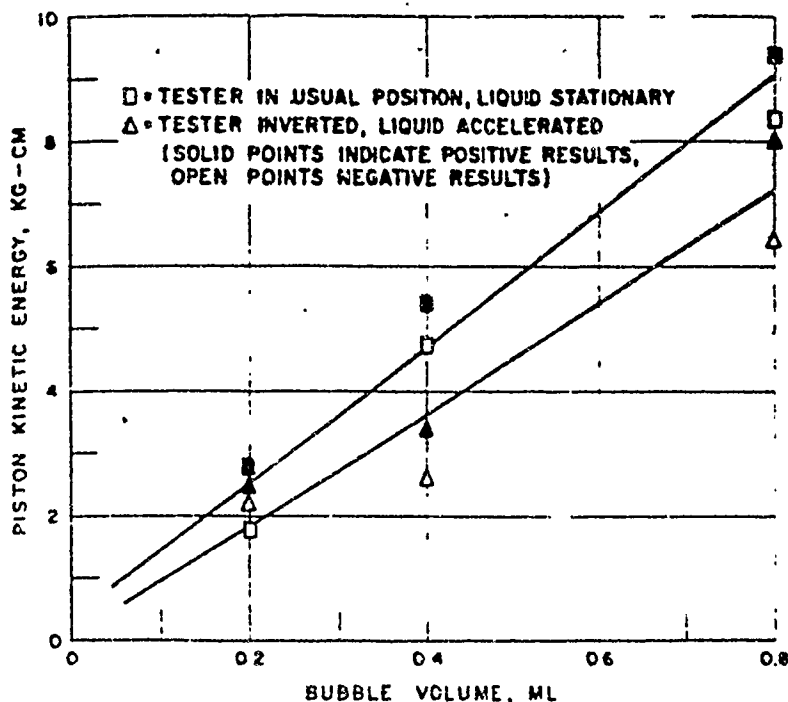

Fig. 10 Sensitivity of nitromethane

"Effects of Gas and Liquid Properties on Detonation-Wave Parameters in Liquid Bubble Systems," A. V. Pinaev and A. I. Sychev, Combustion, Explosion and Shock Waves, pp 735-742, May 1988.

Optical studies have shown that surfaces are unstable during collapse which can be due to bubble interaction in the wave or instability in the collapse (Taylor). The compression distortions increase as viscosity decreases at higher temperatures, which increases effective surface area, which increases the heat loss from the gas heated by compression and ignition, so detonation velocity is reduced. The temperature rise in the bubbles falls as viscosity decreases, as the compression differs substantially from adiabatic, depends on the rate of collapse, and the ignition delay increases exponentially and can even prevent ignition. JH: Note idea that surface breakup works against ignition; but once ignition does occur the high surface area should accelerate growth. Low viscosity is said to be critical to surface breakup and will show up at the higher temperature; its effect is to work against ignition. At the lowest temperature (of liquid) viscosity is high and surface breakup is reduced; but the entire story requires including compressibility which affects rate of collapse. This was not done. Need studies versus temperature for NM (no NM in this study), where all mechanical properties enter simultaneously. This paper based on high detonation velocity as altered by collapse of contained bubbles. Hence it is for LVD. Note that ignition also depends on viscosity which is relevant to hazard. It is not clear at what temperature hazard is greatest, but see (29).

76/378

"Detonation Transformations in an Aerated Liquid," B. N. Kondrikov, G. D. Kozak, V. B. Oblomskii, and A. V. Savkin, Combustion, Explosion and Shock Waves, pp 195-202, March/April 1987.

Porosity $m = 1 - \rho_o/\rho$ characterizes the degree of aeration where ρ_o and ρ are the densities of the sample and homogeneous liquid. Low velocity detonation of NM with m = 0 did not occur and is reported to only occur in thick-walled glass tubes. Low velocity propagation is cut off for sample density (ρ_o) greater than 1.09 g/cm^3. JH: For example, more porosity needed for low velocity propagation.
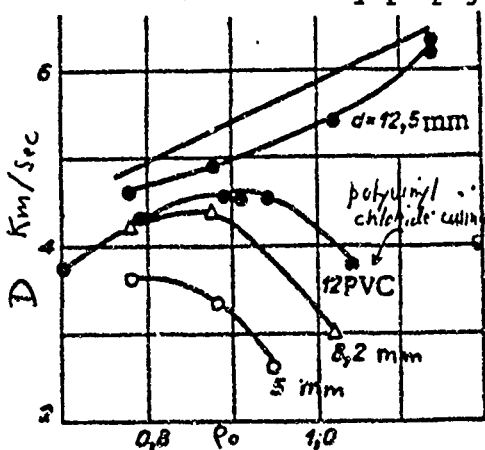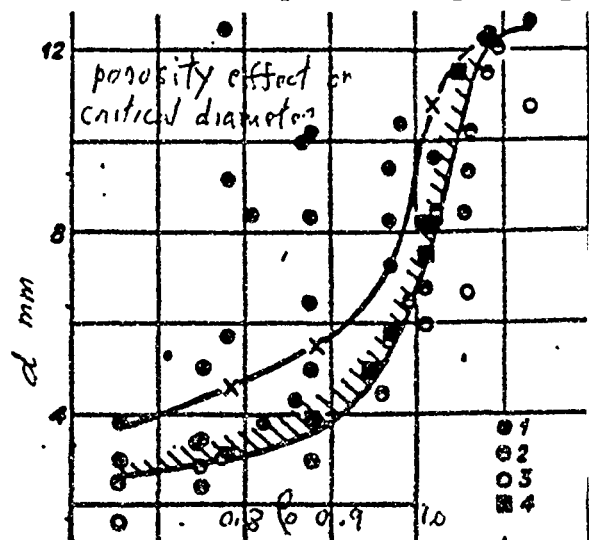
As porosity decreases (ρ_0 increases) the critical diameter (minimum for propagation) increases as shown above and simultaneously D increases toward the high velocity value as seen above. Critical diameter curves are seen below as plots of detonation velocity versus 1/d (mm^{-1}) where ρ_0 has value for curves 1-0.66, 2-0.78, 3-1.01, 4-1.10.
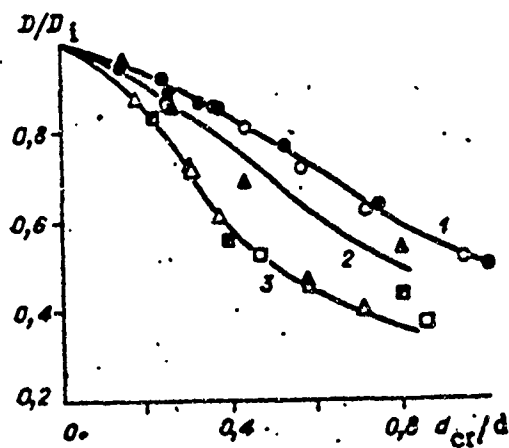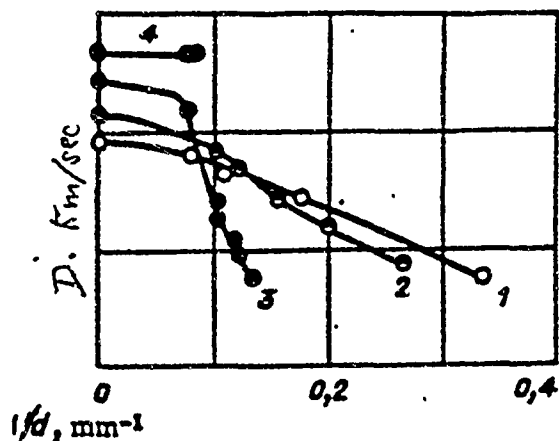
"For LVD, the main regime of the process is combustion of a liquid which has become inflamed as the result of compression of a gas bubble in a shock wave. Approximate calculations show that for a low viscosity liquid, the main source of heating and inflammation in a comparitively weak shock wave is adiabatic compression of the gas in the flow behind the shock wave." **JH: Note that the previous reference (75) said that at low viscosity surface breakup acts against ignition and growth . Here the opposite is asserted, but a weak shock wave is specified. It follows that it is believed that for a weak shock wave, surface breakup does not dominate.** "The possibility that fragmentation of the liquid in the shock wave into small drops or a gas bubble into smaller bubbles . . . requires further study."

d* are points of inflection in curves of porosity effect on critical diameter. D_i is infinite diameter detonation velocity. Curves show how D/D_i decreases as d decreases toward $d_{critical}$, i.e.,

$$\frac{d_{critical}}{d} < 1 \qquad \text{As d approaches } d_{critical} \qquad \frac{d_{critical}}{d} \text{ approaches 1.}$$

77/376

"Structure and Properties of Detonation in a Liquid-Gas Bubble System," A. V. Pinaev and A. I. Sychev, Combustion, Explosion and Shock Waves, pp 360-368, November 1986.

These authors have a more recent paper (75)/(375).

The detonation wave propagates by igniting bubbles radiating shock waves into the surrounding liquid which in turn ignites bubbles ahead of the

wave. "Generally speaking, bubbles in the liquid have a nonspherical form, but with increase in liquid viscosity they become close to spherical." After ignition, the bubbles expand and radiate a shock wave followed by rarefaction zones in which a large number of fine bubbles are found. **JH: Since viscosity increases at the low temperature extreme, the bubble collapse becomes spherical and rate of temperature rise within depends on compressibility and diffusivity.**

78/377/651

"Detonation Waves in a Liquid-Gas Bubble System," A. I. Sychev, <u>Combustion, Explosion and Shock Waves</u>, pp 365-372, November 1985.

This author is coauthor in two more recent papers (75) and (77).

Describes equipment for creating a column of liquid containing bubbles and studying shock wave propagation including instrumentation used.

Referring to adiabatic compression by a shock wave, he notes that "if a bubble is not ignited upon compression before formation of a cumulative jet, subsequent ignition of the explosive mixture in the bubble is possible upon propagation of the liquid jet."

Regarding possible bubble interaction, he finds that the region of hot gas mixture explosion products in the bubbles does not exceed 6 d_o while the mean distance between bubbles in the case photographed was 2.3 d_o. **JH: A jet in a bubble occurs when the collapse is due to a planar shock on a spherical bubble. For compression due to slow rise of pressure, a spherical collapse is more likely with bubble surface breakup also a possibility, but not formation of a Munroe jet.**

79

"Shock-Wave Ignition of Liquid-Gas Bubble Systems," A. I. Sychev, <u>Combustion, Explosion and Shock Waves</u>, pp 250-254, September 1985.

This author is involved in three more recent papers (75),(77), and (78).

He distinguishes four types of chemically active systems: I. non-reacting liquid-active gas bubbles; II. liquid fuel-oxidant gas bubbles (or opposite phases); III. active liquid-nonreacting gas bubbles; IV. active liquid-active gas bubbles. For III and IV, he cites a reference in Russian (A. V. Dubovik and V. K. Bobler, "Shock Sensitivity of Liquid Explosive Systems," Nauka, Moscow, 1978) but note that these authors have an earlier paper in English (77). This paper is devoted to categories I and II.

Pressure fluctuations are a consequence of oscillations of the gas bubble; after compression in the shock wave the bubble begins to expand, radiating a pressure wave into the ambient medium. If during compression

ignition of the bubble occurs, the pressure of the gas in it increases which can lead to intensification of the radiated pressure wave. Pressure fluctuations are absent in a liquid without bubbles.

80/381

"On the Mechanism of the Reaction "Hot Spots" Origin at Liquid Explosives Detonation," A. N. Dremin, V. Yu. Klimenko and I. Yu. Kosireva (USSR), Eighth Symposium (International) on Detonation, pp 678-687, 1985.

Describes an "accumulation" mechanism in which translational modes are excited first, then redistributed to vibrational modes, and if the rate of energy flow into the latter exceeds a relaxation process, energy density rises. But states "the mechanism does not come into action if the molecules are small like NM molecules." Investigates the alternate proposed mechanism that overheated micro-regions due to shock interaction with density discontinuities are source of initiation in wave. Does calculation to show that this interaction leads to magnified regions of high temperature, validating the model. Notes that the whole actuation process will accelerate--if the characteristic time of their development is comparable or smaller than the characteristic life time of the overheated regions. JH: This paper is primarily a Category 3 paper. However, there is an analogy to be drawn regarding adiabatic compression of bubbles. On a larger scale there are macroregions whose role depends on the characteristic time of development exceeding transport of generated energy away from the site (and the energy released by reaction. This highlights the importance of rate of compression.

81

"Shock Waves in a Liquid Containing Gas Bubbles," V. K. Kedrinskii, Combustion, Explosion and Shock Waves, pp 495-504, March 1981.

If the linear scale of the wave is much greater than the bubble radius, and if the collapse time of the bubble is greater than the time for the wave to traverse the bubble, then the bubble dynamics is investigated in a spherically symmetrical setting, which is a significant simplification. JH: Note that during the collapse of the bubble, the driving pressure may be changing which must be taken into account. Note also that this ignores the surface instability (Taylor) that can lead to loss of spherical symmetry. In the presence of an initial translation velocity, the collapse of the bubble in an ideal liquid differs substantially from the case where its center is stationary during the entire pulsation process. JH: Obviously the difference depends on how high the translation velocity is compared to collapse rate (i.e., the displacement of center during oscillation). When translation exists, kinetic energies of radial and translational motion are redistributed in favor of the latter. Does supporting calculations and cites reference. Continues with material relevant to bubble screens against shock waves. JH: Basis is here for considering parameters regarding water-hammer situation.

82

"Effect of Initial Temperature of Certain Explosive Liquids on Their Sensitivity to Explosion Excitation by Cavitation." V. Ye Gordeyev, Yu. S. Matveyev, Combustion, Explosion and Shock Waves, 5, No. 4, pp 406-407, October - December 1969.

Proposes that, "The temperature of the compressed vapor should be the higher the greater the ratio of the collapse pressure to the initial vapor pressure. Since cooling reduces the vapor pressure, while heating raises it, it may be assumed that cooling the liquid will increase the vapor temperature in the collapsing cavities and heating reduces it. Hence, heating should reduce, and cooling should increase, the effectiveness of cavitation as a means of initiation." JH: This agrument cannot be ignored. No experiments or calculations were done for NM. Obviously, other parameters that are also temperature dependent have been ignored, e.g., vapor pressure, viscosity, compressibility, surface tension, chemical reaction. This points out need to use a full model, such as that of PCRL for calculations and experiments directly on NM as a function of initial temperature and the stimulus profile. Showed a case where heating a solution prevented inducing an explosion due to the increase in vapor pressure.

83

"Adiabatic Thermal Explosion of Entrapped Gas in Liquids," Yu. M. Volynskii-Basmanov and V. I. Kuz'min, Combustion, Explosion and Shock Waves, 4, No. 1, pp 29-31, 1968.

Provides a system of differential equations for investigating the adiabatic compression and thermal explosion of a gas bubble in a liquid. Considers a compressible liquid with bubble small enough that pressure difference across bubble can be neglected, but large enough to disregard heat conduction processes. Does the mathematics to show the consequences of the equations. Shows a response that oscillates across to the applied stress wave alternately transferring energy from the liquid to the bubble and vice-versa. JH: This paper confirms the importance of including the liquid compressibility in any model of bubble collapse. Results should be compared with those of PCRL. See (33).

84/382

"Determination of the Critical Shock Initiation Conditions for Homogeneous Explosives," I. M. Voskoboinikov, V. M. Bogamolov, and A. Ya. Apin, Combustion, Explosion and Shock Waves, 5, No. 4, p 323, 1969.

Decomposition kinetic must be obtained on the homogeneous liquid which can be done most readily in shock-compression experiments because one can get to the p, v, T state of interest in times in which substance is unable to undergo chemical reaction and create that state over a significant volume. The state is maintained for so short a time that transport can be neglected.

JH: For our use the assumption must be made that kinetic pathways and rates so determined can be extrapolated down to adiabatic compression of a bubble over a longer time at much lower pressures. His calculations, "neglect burnup of the explosion during the adiabatic explosion induction period." For liquid NM, the critical pressure for a shock-initiation is 93 Kbar experimentally (ref cited) and author calculates 115 Kbar. The ignition lag is given as 1 microsecond for this shock with temperature rising to 1200 K. JH: Value of ignition lag entirely different for bubble collapse—this is all for <u>homogeneous</u> liquid. Other references go as low as 85 Kbar for shock initiation in homogeneous NM.

85/383

"Initiation and Development of Detonation as a Result of the Action of Weak Shock Waves on Liquid Explosives," A. V. Dubovik and V. K. Bobolev, <u>Combustion, Explosion and Shock Waves</u>, <u>5</u>, No. 3, p 245, 1969.

For excitation of explosion by weak shocks (1 - 10 Kbars), shock heating of the liquid is not more than 100°C; gas bubbles, impurity particles must act as "hot spots." Liquids have little resistance to negative stresses and therefore cavitate. This mechanism acts as the propagating factor for low veloc.ty detonation by presence of a precursor wave of cavitation. Precursor can be achieved by sound speed in material of vessel exceeding weak shock velocity on other conditions that create a cavitated state, e.g., barriers, change in direction leading to rarefaction waves. Low velocity detonation could not be initiated in NM using a weak explosive as initiator. If NM is exposed first to a weak (about 1 Kbar) and then a stronger (about 50 Kbar) shock, the liquid does explode. JH: **An initiating system might be designed to do this to assure reproducible initiation of NM in the TEXS application.** NM in a vessel measuring 3.5 x 5 cm and 5 cm tall with thick Plexiglas walls, did not, in homogeneous state, initiate with a 50 Kbar shock. If, however, a metal (or glass) plate is placed a small distance above the NM, the impact of the ejected liquid against this surface leads to explosion. JH: **Another form of energy concentrator.** A layer of NM 25 mm thick was introduced between thick Plexiglas plates to form a charge 50 mm wide and 105mm thick. Cavitation was produced by exploding a weak charge on top of the NM. The initiating shock generator at the bottom provided 50 Kbar after a delay. Low velocity detonation, or a strong shock wave supported by reaction, was propagated at 2450 m/sec. Near the end of the charge the wave velocity was 1700 m/sec. Attenuation of the reaction wave in NM is attributable to poor support from the interior of the wave, where the slow reaction apparently ceases immediately after penetration of the rarefaction wave into the reaction zone. JH: **Low velocity detonation has a very long detonation zone.** Hence geometry effects and confinement can easily alter the velocity of propagation and even lead to quenching if the liquid the wave is entering has reduced cavitation. For adequate diameter confinement and booster, the NM should detonate high order which is essential to achieve the required performance of NM for TEXS.

"Critical Phenomena in the Detonation of Liquid Explosives," A. N. Dremin, Twelfth Symposium (International) on Combustion, 1968.

It was found (refs cited) that the front of a detonation wave in NM was rough and that the chemical reaction at the detonation front did not occur simultaneously. For some other explosives, e.g., NG and TNM, it is smooth. The ratio for the induction period τ to the overall reaction time Δt representing considerable heat release underlies stability of the detonation front. Thermal theory implies that $\tau/\Delta t$ strongly depends on activation energy, heat of explosion, initial temperature of chemical decomposition with ratio tending to unity as the first two go higher or the last lower. For $\tau/\Delta t \sim 1$ tends to be unstable; if $t/\Delta t$ is low, the detonation front tends to be stable. Since charge sizes are finite, limiting initiation conditions depend on $t/\Delta t$ Since shock compression of booster will die off, if $t/\Delta t$ is large, initiation may not occur or rarefactions will enter before a steady state can be achieved. This determines threshold for shock initiation. For $t/\Delta t$ large, local adiabatic explosions control the frequency of the detonation front pulsations (JH: **Dependence on local sites-heterogeneity**) and the scale of its nonuniformity. For weak explosives with an unstable front of the NM type, breakdown of the reaction occurs at the front of the lateral rarefaction wave.

"Sensitivity of Some Explosives to Shock Wave," V. S. Ilyuklin and P. F. Pokhil, Dokl, Akad, Nauk, SSSR, 140, pp 179-180, 1961. (Translation appears as p 129, 130), C.A. 56, 6229h, 1962.

Detonation wave was transmitted through a copper barrier varied from 5 to 30 mm as a type of gap test. For various explosives, Table 1 gives the minimum (critical) pressures in the front of the initiating wave corresponding to maximum delay of detonation. JH: **This data is a point on "Pop plot."** Relative values, those to left of vertical line, have the higher values associated with homogeneous explosives. These relative values can be changed by increases in size of donor and acceptor and confinement (by a factor of about two).

Explosive	HMX	Cast TNT	Liq TNT	NG	NM	Pressed TNT	Pressed HMX
Density g/cm^3	1.80	1.62	1.46	1.60	1.14	1.63	1.74
P critical (Kbar)	10	11.5	11.0	8.5	9.0	2.2	1.5

Estimated that at 0.1 Kbars, the adiabatic compression temperature (ref cited) is 700 - 800°C which evidently is sufficiently high for rapid ignition of the explosive. But 0.01 - 0.02 Kbars corresponds to a temperature rise

below 100°C and ignition may only result by presence of energy concentrators (heterogeneous case). **JH: Pressures quoted seem low for shock initiation of high order detonation.**

88

"Critical Energy of the Excitation of an Explosion by Impact in Different Explosives," M. Ya. Vasil'ev, Detonatsiya, Mater. Vses. Simp. Goreniyu Vzryvu, 6th Editor Dremin A.N., pp 65-68, 1980, In Russian. Publisher Akad Nauk, SSSR Inst, C.A. 95:100043w.

The title energy was detd. in trotyl, tetryl, octogen, hexogen, NH_4ClO_4, tech. $MeNO_2$, and distd. $MeNO_2$ with the explosions initiated by impact of a flat steel plate with a given speed and mass. The results are tabulated and high-speed photographs of the detonation of $MeNO_2$ and NH_4ClO_4 are reproduced. **JH: Dremin is well known for careful well thought out studies. This reference falls between two others in English; (86) in 1968 and (80) in 1985. It does not include NM. It should be pursued only if other references need clarification.**

89

"Study of Hydraulic Shock in Hydrodynamic Shock Tubes," B. E. Gelfand, E. I. Timofeev, Inst Khim Fiz, Moscow, USSR, Teplofiz Vys Temp, 1983, 21(2), pp 330-334. In Russian. C.A. 99:7468m

Expts. were carried out on pressure fluctuation in a 2-phase (gas-liq.) medium when a const. pressure was applied on the surface. The pressure pulsation is assocd. with the multiple paths of compression and rarefaction waves. The period and the intensity of vibration depend on the compressibility of the medium. The dependence of the damping of velocity oscillations on the volumetric concn. of the gas and vapor $\colon$ water was detd. A correlation is developed for the pressure coeff. after reflection of the wave. **JH: Note importance of compressibility of medium, damping of oscillations described. Gelfand has another paper only in Russian (92).**

90

"Development of a Reaction in Compression-Loaded Nitromethane and Tetranitromethane," A. A. Vorob'ev, Fiz-Khim Protessy Gazov. Kondens. Fazakh Editor V. N. Kondrat'ev, 109 pages, 1979. In Russian. Publisher: Akad Nauk SSSR Inst. Khim Fiz, Chernogolovka, USSR. C.A. 93:149526d

Reaction foci of 1000 A and ~2 mm were found in shock wave studies with $MeNO_2$ and $C(NO_2)_4$, resp. These foci suggested a nonthermal mechanism.

JH: Details of value since NM tested. From abstract one does not know nature of compression loading, but 2 mm bubbles are significant.

91

"Kinematics of a Gas Bubble in a Liquid in the Presence of a Strong Acoustical Compression Wave," Yu. P. Grebenkin and V. M. Kryachko, In Russian. English abstract in Vestn. Leningr Gos, Univ. Ser Fiz Khim, 22, No. 4, 79, 1978.   C.A. 90:1277960

An app. working at acoustic pressures of 0.6 - 105 atm is described in detail.   High-speed photog. was used to study the behavior of the bubbles. Motion and deformation of bubbles in glycerin depend strongly on the acoustic pressure.

JH: This paper appears to be of secondary importance.   Details could not be used to check a theory at low pressure limit.   Acoustic wave effects are described in (63).

92

"Influence of Gas Density upon Splitting of Gas Bubbles," B. E. Gelfand, S. A. Gubin, R. I. Nigmatu, Academy of Sciences USSR Proceedings, In Russian, Dokl. Akad Nauk SSSR, 235, No. 2, 292.

93

R. I. Solaukhin, Academy of Sciences USSR Proceedings, In Russian, Dokl Akad Nauk SSSR 136, No. 2, 311, 1961.

94

V. K. Kedrinskii and R. I. Soloukhin, Journal of Appl Mech and Technical Physics, Zh Prikl Mikh Fiz, No. 1, 27 , 1961.

CATEGORY 3

DETONATION

301/13/635

"Initiation and Growth of Detonation in Liquid Explosives," F. C. Gibson, C. R. Summers, C. M. Mason, and R. W. Van Dolah (BuMines), Third Symposium on Detonation, pp 436-454, 1960.

302/17/639

"The Effect of Physical and Chemical Properties on the Sensitivity of Liquid Explosives," J. E. Hay, J. Ribovich, F. H. Scott, and F. C. Gibson (BuMines), Fourth Symposium (International) on Detonation, pp 412-425, 1965.

303/14/636

"Detonations in Liquid Explosives - The Low Velocity Regime," R. W. Watson, C. R. Summers, F. C. Gibson, and R. W. Van Dolah (BuMines), Fourth Symposium (International) on Detonation, pp 117-125, 1965.

304/15/637

BuMines Quarterly Reports on Sensitivity of Propellant Systems, January 1, 1966 - March 31, 1966, Quarter #6, "Initiation Mechanism," April 1, 1966 - June 30, 1966, Quarter #7, "Theoretical Studies on Bubble Compression and Growth," PA U110 487.

305

"Dark Waves in Liquid Explosive Systems: Their Role in Detonation Failure," Richard R. Watson (BuMines), Fifth Symposium (International) on Detonation, pp 169-174, 1970.

306

"The Stability of Low-Velocity Detonation Waves," R. W. Watson, J. Rebovich, J. E. Hay, and R. W. Van Dolah (BuMines), Fifth Symposium (International) on Detonation, pp 81-86, 1970, with discussion.

307/18

"On the Mechanism of Low Velocity Detonation in Liquid Explosives," Robert F. Chaiken (BuMines), Astronaut Acta, 17, pp 575-587, 4-5 October 1972.

308/16/638

"Initiation of Detonation in Insensitive Liquid Explosives by Low-Amplitude Compression Waves," J. E. Hay and R. W. Watson (BuMines), Sixth Symposium (International) on Detonation, pp 115-123, 1976.

309/19/640

"Effect of Cavitation on the Shock Sensitivity of Liquid Explosives," V. Krishna Mohan and J. Edmund Hay (BuMines), Seventh Symposium (International) on Detonation, pp 373-384, 1981.

310/415/644

"Detonation in Homogeneous Explosives," A. W. Campbell, M. E. Malin, and T. E. Holland (LANL), Second ONR Symposium on Detonation, 1955.

311

"Temperature Effects in the Liquid Explosive, Nitromethane," A. W. Campbell, M. E. Malin, and T. E. Holland (LANL), Jl Appl Phys, 27, p 963, 1956.

312/416/645

"Shock Initiation of Detonation in Liquid Explosives," A. W. Campbell, W. C. Davis and J. R. Travis (LANL), Third Symposium on Detonation, 1960 and Physics of Fluids, 4, No. 4 pp 498-510, April 1961 (essentially the same).

313

"Interaction of a Shock or Rarefaction with a Bubble," N. W. Evans, F. A. Harlow, and B. D. Meixner, Physics of Fluids, 5, No. 6, pp 651-656, June 1962.

314

"Shock and Hot Spot Initiation of Homogeneous Explosives," Charles L. Mader (LANL), Physics of Fluids, 6, No. 3, pp 375-381, March 1963.

315

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"The Detonation of Nitromethane Close to the Limit," A. N. Dremin, G. A. Adadurov, and O. K. Rozanov, Dokl, Akad, Nauk, SSR, Phys Khim, 133, pp 771-773, 1960. Translation

301/13/635

"Initiation and Growth of Detonation in Liquid Explosives, F. C. Gibson, C. R. Summers, C. M. Mason, and R. W. Van Dolah (BuMines), Third Symposium on Detonation, pp 436-454, 1960.

Begins with a summary with reference citations of possible alternate mechanisms to adiabatic compression of contained gas. Did initiation and growth studies in liquid explosives (with test configuration shown in Fig. 1) by shock excitation. Configurations and wall materials were changed in a form of card gap test. Proposes mechanism for initiation of detonation in liquid explosives as cavitation established by shock excitation, possibly with additional heating of the liquid provided by shear forces resulting from differential particle velocities in the liquid and between the liquid and container walls. For a high intensity stimulus, gas bubbles will be formed from the dissolved gases which may first exist as small invisible bubbles of microscopic dimensions. These bubbles, finely dispersed throughout the liquid, constitute weak points as the tensile strength is determined by the largest bubble present. In addition, impurities such as dust particles provide nuclei as do small imperfections in the wall. During cavitation small bubbles may coalesce into larger bubbles of a size sufficient for compression to result in adiabatic heating. Any decomposition of the vapor or droplets in the bubbles which results in the production of gas also results in an increase in bubble size. The time required for the foci to grow through coalescence and reaction may well account for the long delays observed in this initiation process. JH: The sequence describing the role of bubble formation and growth is equally applicable to the point where a stimulus acts on the larger bubbles or created ullage. Whether ignition occurs then depends on the profile of the stimulus and the reactivity of the vapor and liquid as well as the thermal conductivity of both gas, vapor, and liquid and mechanical properties that modulate the adiabatic compression into oscillations at particular rates of compression. For the low velocity detonation model in which the wall carries a precursor shock producing cavitation, the speed of disturbance in the wall material and as a pipe should be established by literature or experiment. This must be compared with velocity in NM and impedances of NM and wall to determine whether a precursor could exist. For performance, one would think that high velocity detonation is desired. However, for cratering, it may very well be that low velocity detonation would be more effective. The selection will depend (if low velocity detonation is feasible) on the mode of initiation. [See (14).]

"The Effect of Physical and Chemical Properties on the Sensitivity of Liquid Explosives," J. E. Hay, J. Ribovich, F. H. Scott, and F. C. Gibson (BuMines), Fourth Symposium (International) on Detonation, pp412-425, 1965.

Some LVD's have a steady propagation rate well above sonic velocity in the explosive and produce well-defined shocks of the order of 5-10 Kbars. Other LVD's have a fluctuating propagation velocity well below the sonic velocity and produce pressures of the order of 2 Kbars or less but no clearly discernible shock wave.

Bulk temperature rise inadequate, hence energy concentrators required. Each element of the liquid must be subjected to two distinct stimuli: a rarefaction which cavitates the liquid, and a shock which causes cavity collapse. JH: **The mechanism applies to local ignition by "water-hammer" compression which can then transform to LVD and possibly to HVD.**

Describes card-gap test for liquids including resistance type probe. Gives results for NM. At 25°C used schedule 40 steel pipe of normal size 1 ½ to 4 inches with 16 inch length, except that 4 inch was 72 inches long. Variations of donor and temperature. Results were ambiguous as shown in Table 2. No appreciable temperature effect was found. Threshold gaps corresponded to shock pressures in NM of about 11.5 Kbars.

JH: **In later papers, the role of the wall in producing a precursor cavitation wave in the liquid was defined. However, data is valid in showing threshold from non-initiation as 11.5 Kbars for shock initiation of liquid at 90°C. See (18).**

"Detonations in Liquid Explosives - The Low Velocity Regime," R. W. Watson, C. R. Summers, F. C. Gibson, and R. W. Van Dolah (BuMines), Fourth Symposium (International) on Detonation, pp 117-125, 1965.

Begins with a summary with reference citations to earlier work on low velocity detonation. Figure 1 provides the geometry for study of low velocity detonations. "Interest in the low velocity phenomenon has developed following recognition that these abnormal detonations play an important part in characterizing the hazards of liquid explosive systems, as demonstrated by the too frequent accidents that have occurred in NG and liquid monopropellant facilities from relatively mild stimuli." LVD "can be initiated by pressures one or two orders of magnitude less than that required for HVD." Concludes "that perturbations of the liquid resulting from precursor wall waves exert a strong influence on the subsequent reactions." For an observer that moves with the reaction, the sequence of events can be visualized as: (a) undisturbed liquid compressed by bow waves derived from the precursor wave in the wall; (b) the compressed fluid begins to move outward where the wall moves outward; (c) liquid cavitates; (d) cavities grow until encounter shocks near reaction zone; (e) cavities collapse, generating high pressures and associ-

ated temperatures that are adequate to initiate chemical reaction. Model for LVD requires that shock velocity in wall be greater than in liquid for stable propagation. **JH: Note that (b) depends on nature of wall; plastic wall moves out more and faster than steel. Also, need wall and liquid properties to support this mechanism.**

Experiments using air-filled hemispherical cavities located on the free surface of fluids, as well as air-filled bubbles in a bulk of liquid explosive, indicate that liquid microjetting may be responsible for the initiation of reaction within the cavities. **JH: For microjetting to be a viable mechanism, a shock must act on a bubble. Mader's work (314) used 95 Kbars; even two orders lower 0.95 Kbars, 950 atmospheres, would be far above pressures to be encountered by any water hammer scenario. This study used a tetryl donor acting through Plexiglas to produce a weak shock.** Authors cite their work in R. W. Watson and F. C. Gibson's, "Jets from Imploding Bubbles," Nature, 204, 4965, pp 1296-1297, 1964. There they used a tetryl donor acting through 0.75-inch thick aluminum on a bubble in liquid. The pressure that acted was 10 Kbar. The pressure at jet impact was estimated as 100 Kbar. **JH: Again note microjetting coincides with at least a weak shock, but could be important for transition process from LVD to HVD. LVD or HVD depends on initiating stimulus.**

304/15/637

BuMines Quarterly Reports on Sensitivity of Propellant Systems, January 1, 1966 - March 31, 1966, Quarter #6, "Initiation Mechanisms," and April 1, 1966 - June 30, 1966, Quarter #7, "Theoretical Studies on Bubble Compression and Growth," PA U110 487.

Input pressure acting on bubble 1.5 Kbars, 1500 atmospheres. Found threshold for EGDN liquid with bubbles containing air, CO_2, and Argon. For latter threshold lower than 1.5 Kbars. A column of gas bubbles is injected into the liquid by means of a No. 27 hypodermic needle having an inside diameter of 0.007 inch. The gas bubble experiments show a trend toward higher sensitivity as the ratio of specific heats of the included gas is increased, which supports the contention that the heat generated by the compression of the bubble contents may be responsible for the reaction. **JH: This conclusion is based on a simple model of bubble collapse and should be compared with the more comprehensive treatment of PCRL authors (32)(33). Also, see (68) regarding gas diffusivity.**

The observation that some degree of reaction takes place below the thresholds suggests that the initial reaction takes place in the vapor and/or droplet field within the bubble. If the rate of release is great enough, the surface of the cavity could then be ignited resulting in a propagating reaction. The reaction would fail to propagate if the energy released was inadequate to compensate for the losses resulting from the heat transferred to the surrounding fluid and the work done in establishing the flow field around the expanding bubble. **JH: This balance is why the rate of bubble collapse (or oscillation) assumes so dominant a role.** Figure 3 shows the arrangement for studying initiation of liquids containing bubbles.

The second progress report provides a theoretical study on bubble expansion due to internal burning. Liquid is assumed incompressible--spherical symmetry used. Designates a volume consumption rate per unit area of bubble surface, u_c, and average molecular weight of products, w, and assumes both ideal gas EOS and isothermal behavior of uniform products within. Then treats special case of stability of bubble expansion versus five different consumption rate expressions. Finds that for greater than a 1.5 power in rate law stable expansion will occur. For LVD, consumption rates are far higher than studied here. For such high rates, expect that turbulence/breakup of liquid would accelerate consumption and lead to LVD to HVD transition. Recognizes that at high pressures, factors neglected or assumptions made would not be valid. **JH: Interesting approach to important role of kinetics in ignition and growth. Vapor concentration at high temperatures would alter burning rate.**

305

"Dark Waves in Liquid Explosive Systems: Their Role in Detonation Failure," Richard R. Watson (BuMines), Fifth Symposium (International) on Detonation, pp 169-174, 1970.

Detonation failure may occur in smaller dimension, e.g. 1 ½ inch diameter, when confined by a wall allowing for an early release wave. This is evidenced by a "dark zone" representing unreacted material. If this extends into the detonation zone sufficiently, failure can occur. For larger diameters and strong confinement, this does not appear to be a problem. Sensitizing and desensitizing agents, added to NM, influence behavior. Concern is with high velocity detonations as evidenced by consideration of induction times for 86 and 201 Kbars. **JH: For TEXS and where HVD is the goal, significance of failure diameter is that if pipe is deformed to a small diameter or not filled at a particular site, failure might occur. The dimensions quoted are such as to make this an unlikely event. It is also important, however, that the initiation system act over a large enough volume of NM since failure could occur by the release waves from the volume not actuated by the initiating system. The volume acted on should be greater than at least 4 cubic inches.**

306

"The Stability of Low-Velocity Detonation Waves," R. W. Watson, J. Rebovich, J. E. Hay and R. W. Van Dolah (BuMines), Fifth Symposium (International) on Detonation (with Discussion), pp 81-86, 1970.

Measured elastic wall velocities and compared with handbook values. Agreed except for polyethylene. (See Table.) "The precise reason for this discrepancy is unclear but may be due to differences in the physical properties of different grades of polyethylene or to nonlinear strain properties in the polyethylene since the stress levels here are much greater than for acoustic waves."

TABLE 1

Observed Wave Velocities for NG-EGDN Undergoing Low-Velocity Detonation
Under Various Conditions of Confinement

Container	V_w	U_d	V_{ext}
Plexiglas	2.2	2.0	1.8
Aluminum	5.1	1.9	5.0
Lead	1.2	1.7	1.2
Polyethylene	1.9	1.4	0.9
Glass	5.0	1.6	5.2

NOTES: (1) All velocities in mm/μsec.
       (2) V_w measured elastic wall wave velocity.
       (3) U_d measured detonation rate.
       (4) Handbook values of extensional velocity.

JH: For TEXS, polyethylene pipe is proposed. If pipe·properties play
a role, that role will also be a function of temperature and should be mea-
sured at temperature extremes to be encountered. "In essence, the reaction
wave, once initiated, consumes that portion of the fluid that has been cavi-
tated by the precursor wave; this reaction is interrupted when the cavity
field is consumed. However, the elastic precursor wave is able to propagate
ahead and create another cavitated region"—so pulsating propagation can
coalesce into stable LVD. "The inherent reaction role of fluid as well as
the sound velocity of the container and dimensions are felt to be important."
A necessary condition for stability is that the detonation wave (for LVD) be
subsonic relative to the wave velocity of the container material. "If this
condition is not met, pulsating detonations will occur as described above,
and also failure may occur depending on the properties related to the support
of the pulsations. A. N. Dremin, in Discussion, added:

It has been shown theoretically that the frequency of natural
vibrations of a thick-walled tube depends on the ratio of the inner to
outer radii and has a maximum at a ratio equal to 0.65 (Ref. 2). From
cavitation theory (Ref. 3) it is known that the resonance size of
gaseous cavities in liquids are determined by the frequency of the
applied ultrasonic field. Here we have an approximately inverse depen-
dence. Bubbles of a size larger than the wave length of resonance do
not disappear. They vibrate intensively and increase in diameter under
the influence of gases and vapors of the liquid. In addition, the
bubble's diameter increases considerably due to coagulation. This
implies that when the vibration frequency of a tube increases, the
number of bubbles in a liquid explosive within also increases.

The bubbles appear behind the elastic wave after a certain time
and their size increase up to the moment of meeting with the detona-
tion front.

Under shock compression of bubbles, the explosion of explosive vapor in the bubbles occurs. The explosion does not spread too far relative to the dimensions of the bubbles. The front of the low-velocity reaction wave does not represent a smooth surface. It is not stationary in time or in intensity distribution. From one bubble to the next, spherical shock waves attenuate rapidly and consequently do not give rise to any considerable reaction in the bulk. The velocity of these waves will, in general, decrease down to the speed of sound of the liquid. This fact is obviously the reason that the velocities of low-velocity waves in all known liquids are only a little larger than the sound velocity.

Ref. 2.J. F. Bird, R. W. Hart, and F. T. McClure, J. Acoust. Soc. of Am. 32, 11, 1404 (1960).

Ref. 3.L. K. Zarembo, V. A. Krasilnikov, Vvedeniye v Nelineinuuyu Akustiku, Isd. Nauka, 262 (1966).

JH: Note that the wall characteristics are important for LVD. The explosiveness of the bubble content will depend on the vapor content of NM. Numbers of bubbles, thermal diffusivity, rate of compression, etc., enter as well.

307/18

"On the Mechanism of Low Velocity Detonation in Liquid Explosives," Robert F. Chaiken (BuMines), Astronaut Acta, 17, pp 575-587, 4 - 5 October 1972.

Abstract--A theoretical description of low-velocity detonation (LVD) in liquid explosives has been developed, based upon a cavitation model of the phenomena. In this model, precursor waves cause cavitation of the liquid; the cavities are then shock-initiated by the advancing detonation front. The Chapman-Jouguet (C-J) condition of classical detonation theory has been extended to this case where precursor wave effects are important. In essence, it is shown that coupling of rate processes through a precursor wave limits the number of Hugoniot adiabat states that are accessible. Thus, the solution to the Rankine-Hugoniot equations for the steady-state detonation velocity involves a minimization of the velocity subject to the constraints imposed by the coupled rate processes.

For the case of LVD in liquid explosives, six rate processes are identified and treated analytically to yield an expression coupling the detonation pressure, extent of liquid cavitation, and wall shock attenuation rate. This expression, along with the applicable jump conditions for the cavitated liquid and an equation of state for the detonation products, yield a quantitative description of stable LVD.

Calculated detonation velocities, pressures, and stability conditions are in very good agreement with the available experimental data for nitroglycerin, ethylene glycol dinitrate, and nitromethane.

JH: This is a theoretical paper on role of precursor cavitation waves in producing low velocity detonation (LVD). Earlier papers develop the qualitative concepts and provide data. Reference (16) disagrees with this one regarding NM and indeed states there is a hazard. Author believes Chaiken did NOT consider interrelation of reaction and cavitation regarding bubble properties.

308/16/638

"Initiation of Detonation in Insensitive Liquid Explosives by Low-Amplitude Compression Waves," J. E. Hay and R. W. Watson (BuMines), Sixth Symposium (International) on Detonation, pp 115-123, 1976.

JH: This paper is closest to TEXS application. An experiment devised to simulate the development of explosive reaction in a large mass of cavitated liquid is described in which a massive steel piston is propelled into a container (diameter 10 cm) filled with a liquid explosive into which bubbles have been introduced. In this experiment, transition to "detonation" has resulted using nitromethane and other marginally detonable liquids at initial piston velocities of 24 to 90 meters per second. With further increase in scale size, abrupt accelerations of the order of those occurring in transport may suffice to produce explosion. JH: This is closest to TEXS application.

A mathematical model is described by which the hazard potential of deflagration-to-detonation transition in large masses of a reactive liquid subjected to cavitating conditions and pressure surges can be assessed from buring rate data or from small-scale experiments such as that described.

Begins with a critique of Chaiken (18) whose results tend to indicate that the possibility of LVD in NM is marginal. Attributes his result to the large value of the calculated cavitation rate constant which leads to decoupling of cavitation and reaction processes. Describes test for development of explosive reactions in liquids by weak stimulus (<1 Kbar). Projectile driven by compressed air moves down a steel barrel (10.2 cm i.d., 3.3 m long). The minimum criterion for explosion is cylinder unfolded or in pieces, significant blast, and complete consumption of the liquid. Bubble field in liquid with diameters in the range of 0.05 to 0.2 cm and density 0.5 to 10 cm^{-3}. In earlier work it was found that for NM initiations could not be obtained with the highest velocity when only one or a few large bubbles were present. The impact of the projectile on NM at the highest velocity produces about 2.5 Kbars. The threshold velocity for NM was 24 ± m/sec. Comparison with other liquids, on the basis of thresholds and literature burning rates, suggest that those systems that have burning rates less than about 0.13 cm/sec at 11 MPa do not seem to explode at the highest velocity of this test, and those with rates substantially greater exploded at

lower impact velocities. Value for NM = 0.27. **JH: NM does explode at 24 ± 2 m/sec if bubble profile is present.**

Presents a simplified model with incompressible liquid (considers value for less than a few Kbars), spherical symmetry, Abel equation of state, isothermal expansion, and some simplifying mathematical assumptions. Derives bubble pressure versus time as a function of parameters (Fig. 2). Finds development of explosive reaction is very sensitive to the burning rate parameter, somewhat sensitive to bubble dimensions and density and importantly with scaling upward. In Discussion, R. I. Solouklin suggests that effect of assymmetric collapse must also be taken into account.

309/19/640

"Effect of Cavitation on the Shock Sensitivity of Liquid Explosives," V. Krishna Mohan and J. Edmund Hay (BuMines), Seventh Symposium (International) on Detonation, pp 373-384, 1981.

Describes the gap test for cavitated liquids. Shock sensitization due to cavitation is observed for NM, the threshold shock pressure changes from 80 Kbars to 7 Kbars with cavitation added by air bubbles. Propagation velocity was about 2600 m/sec for cavitated liquid (uncavitated 6320 m/sec). Shock sensitivity is affected by the γ value of the gas with NM. Higher threshold values are obtained with argon ($\gamma = 1.67$) and the reverse for propane ($\gamma = 1.13$) compared to those observed with air and nitrogen ($\gamma = 1.40$). Threshold gap values are enhanced with oxygen (even though gammas are about the same as nitrogen and air). Diluents such as benzene or acetone desensitize NM at low diluent concentrations. Tests were done that demonstrated that "gas bubbles govern the initiation characteristics of NM." Vapor pressure of NM is given as 30 mm.

Wall has role in creating precursor, but also governs time that the dynamic pressure is maintained in the reaction zone, cavitating to driving reaction to completion.

JH: All the qualitative features are brought together. Need gamma for high vapor content of NM. Note threshold for shock initiation and detonation velocities given for LVD and HVD.

310/415/644

"Detonation in Homogeneous Explosives," A. W. Campbell, M. E. Malin, and T. E. Holland (LANL), Second ONR Symposium on Detonation, 1955.

Used NM in 55 gallon drums from Commerical Solvents specified as NM by weight minimum 95, Nitroparaffins 99, Specific Gravity 25/25°C 1.1283, Acidity as acetic acid 0.01, Water 0.052. "To further guard against the presence of alkaline materials which might act out as sensitizers, the NM was redistilled at reduced pressure from sulfuric acid and stored in glass bottles." The temperature (°C) dependence of density given by $d_T = 1.1645 -$

1.337 x 10^{-3} T - 1.15 x $10^{-6}T^2$ + 3.81 x $0^{-9}T^3$. Raising temperature increases detonation velocity <u>but</u> decreasing density decreases detonation velocity for liquid explosives. The combination results in NM in a decrease of -3.7 m/sec/°C with increase of T. Provides data on diameter effect in NM versus T in glass tubes and for the failure diameter. For latter, over the range - 12°F to 98°F the failure diameter varied from 15 mm to 35 mm, increasing as the initial temperature was lowered. **JH: Thus for HVD below 1-½ inch at - 12°F, failure to propagate would occur. For TEXS at low T limit, a constriction to 2 inch diameter must be avoided.** "Plastic tubes were not used because of the possibility of contamination of the explosive by solvent action." **JH: Is this a problem with polyethylene tubes used for TEXS?** "Failure occurred by non-luminous areas spreading inward from the confining walls and choking off the detonation process." Provides test configurations for liquids for detonation velocity, diameter, and confinement versus temperature.

311

"Temperature Effects in the Liquid Explosive, Nitromethane," A. W. Campbell, M. E. Malin, and T. E. Holland (LANL), <u>Jl Appl Phys</u>, <u>27</u>, 963, 1956.

Detonation velocity and failure diameter are strongly dependent on the initial temperature of the NM. The velocity dependence is -3.7 m/sec/°C. The failure diameter for NM measured in glass tubes increased by a factor of two as the initial temperature is lowered approximately 60°C. Values shown in Figure 2 for fai·_re diameter in glass tube range from 1.5 cm at 35°C to 3.5 cm at -25°C. **JH: For the detonation to fail in the TEXS application, it would take a constriction to 1-½ inch diameter at the cold temperature extreme.** See another paper by same authors (310).

312/416/645

"Shock Initiation of Detonation in Liquid Explosives," W. W. Campbell, W. C. Davis, and J. R. Travis (LANL), Third Symposium on Detonation, 1960, and <u>Physics of Fluids</u>, <u>4</u>, No. 4, pp 498-510, April 1961 (essentially the same).

"Nitromethane and other explosives in the homogeneous state are initiated as a result of shock heating. The initiation process is essentially a thermal explosion. The shock heated explosive reacts very slowly at first, but the reaction rate accelerates due to self-heating and detonation results. This detonation wave overtakes the initial shock wave and temporarily overdrives detonation in the unshocked explosive ahead of it." The induction time (between entrance of initial shock and initiation) varied from 5.0 microseconds at NM temperature of 1.7°C to 0.45 microseconds at 45.5°C. The shock pressure was about 90 Kbar. **JH: This is the definitive comprehensive paper, referred to by all on <u>homogeneous</u> detonation. Fortunately it was done on NM. Therefore, it has all forms of data on HVD of NM. It also gives the experimental procedures used and earlier references.**

Also investigated initiation of bubbles of various gases. Here, the major effect appeared to be shock wave interactions due to presence of bubbles; therefore, solid objects were also introduced into the NM. This area is better treated in later IANL and BuMines papers.

313

"Interaction of a Shock or Rarefaction with a Bubble," N. W. Evans, F. H. Harlow, and B. D. Meixner (IANL), Physics of Fluids, 5, No. 6, pp 651-656, June 1962.

The presence of a sufficiently large bubble of gas or piece of tungsten or plastic, decreased the induction time by a time that was insensitive to material. JH: **This is effect on a strong shock. It is an effect different than adiabatic compression. It only enters TEXS possibly for transition from LVD to HVD or for problems initiating NM high order with a bubble.** This is a complete study showing bubble collapse for a strong planar shock. JH: **Interesting, but can be skipped regarding TEXS. The next paper by Mader (314) is more comprehensive.**

314

"Shock and Hot Spot Initiation of Homogeneous Explosives," Charles L. Mader (IANL), Physics of Fluids, 6, 3, pp 375-381, March 1963.

This study confirms the mechanism for initiation of homogeneous explosives (neat NM) to within experimental error going beyond qualitative agreement. Initiation of inhomogeneous explosives (NM with bubbles, objects, etc.) cannot result only from the mean shock heating, but rather that shock interaction with the inhomgeneities produce numerous hot spots in the bulk of the shocked explosive from which thermal decomposition may proceed. ("Hot spots," "local sites," and "energy concentrators" are synonyms for this.) The progressive release of energy from these hot spots may strengthen the shock sufficiently to cause eventual initiation of detonation.

For a bubble in NM, it was observed that a shock that was too weak for immediate initiation, interacting with a bubble of sufficient size, produced a hot spot in the liquid explosive just beyond the bubble that would initiate detonation in approximately 0.1 μsec. Bubbles smaller than a critical size (~0.03 cm radius) failed to initiate propagating reaction. Critical size was nearly independent of bubble material. JH: **This is at ~95 Kbars shock level. Mechanism not directly applicable to TEXS.**

315

"Experimental Observations of Initiation of Nitromethane by Shock Interactions at Discontinuities," J. R. Travis (LANL), Fourth Symposium (International) on Detonation, pp 386-393, 1965.

The induction time for inhomogeneous explosives, such as NM with inclusions, depends on the size and material of the solid inclusion. The quantitative description requires knowledge of the complex shock interactions peculiar to each case. For shock less than 80 to 90 Kbar, detonation does not occur for these experiments because the geometry permits side rarefactions to enter so induction times >8 μsec cannot be determined. No simple relationships between initiating efficiency and shock properties were found, but shock interactions are considered the dominant mechanism. However, "no material has been found that can be inserted as an inclusion with a minimum dimension greater than 0.1 mm which will not cause early initiation in its neighborhood" independent of impedance and true for impedance even close to that of NM. Aluminum had unusual efficiency in causing initation, suggesting there was some surface effect. **JH: This is the key experimental paper on inclusions in NM, but it is for strong shocks and, therefore, not relevant for TEXS unless used for a method to achieve assurance of initiation.**

316

"Initiation of Detonation by the Interaction of Shocks with Density Discontinuities," Charles L. Mader (LANL), Physics of Fluids, 8, pp 1811-1816, 1965.

For hot spots, two competing processes occur just outside the hot spot for strong shock. The first process is expansion resulting from the divergent flow of the heated fluid which tends to cool it. The second process is chemical decomposition of the fluid which tends to heat it. Propagating detonation occurs only if the second process dominates. Did two-dimensional hydrodynamic calculations for shock interacting with spherical void and aluminum cylinder. Shows computer sequential photos of the collapse of the spherical void and intraction with the aluminum cylinder. For example, a 25 Kbar shock in NM interacting with a 0.02 cm radius void results in a hot spot which decomposes but fails to initiate propagating detonation. Another example shows failure to buildup to propagating detonation from a 85 Kbar shock interacting with a 0.032 by 0.002 cm radius cylinder of aluminum in nitromethane. Quotes reference for experimental results that critical cylinder radius for 85 Kbar is greater than 0.005 cm, which agrees. **JH: This work does not appear directly relevant to TEXS. One must be aware that shock interaction can produce higher pressures, but the domain of 25 Kbar is way out of range.**

317

"Single and Polycrystalline Effects of the Shock Sensitivity of Explosives," John B. Ramsey (LANL), Report of Working Group Meeting on Sensitivity of Explosives, CEIR, NM Tech Socorro, 15-18 March 1987, pp 712-733.

This paper does not include NM. It repeats the now known difference in mechanisms for shock (strong) initiation of homogeneous and heterogeneous materials. For the latter, the concern is with solids and factors that make them different such as exact details of micro- and macro-crystal morphology, percent voids, inter-crystalline matrix, chemical purity, and type of insult (projectile, impact, shock, etc.).

Only information on NM is on page 719. "Addition of SiC changes homogeneous initiation of NM at 8.5 GPa (85 Kbar) to heterogeneous initiation at 2.3 GPa (23 Kbar)." Nature of wave history is also affected.

JH: **Regarding TEXS vulnerability, the presence of sand suspended in NM would sensitize it as described.**

318

"Effect of a Physical Inhomogeneity on Steady-State Detonation Velocity," Ray Engelke (LANL), Physics of Fluids, 22, (9), pp 1623-1630, September 1979.

Physical inhomogeneities produce flow modifications that create localized hot regions. These local hot regions apparently produce an effective chemical reaction rate which allows a stable propagation at a reduced charge size. Confined NM in glass tubes and added silica impurities with a known particle size distribution, and used guar gum to hold silica in suspension. The failure diameter reduced from 16.2 mm to 9.6 mm. The pyrex tubing was 1.2 mm thick, which for a reaction zone length for NM of 200 μm (experimental value), is effectively infinite confinement regarding detonation. In Figure 6, curves for detonation velocity versus 1/R are given for NM and NM with silica. An equation with included constants for the diameter effect is also provided. JH: **It follows that a small amount of sand does not seriously alter detonation velocity. However, it may also alter sensitivity in the TEXS application. This is one of a series by this author. See (319) and (320).**

319

"Effect of a Chemical Inhomogeneity on Steady State Detonation Velocity," Ray Engelke (LANL), Physics of Fluids, 23, (5), pp 875-880, May 1980.

JH: **This paper is included because it is one of a series. It deals with sensitizers which are NOT used in TEXS. However note that an undesired impurity could turn out to be a sensitizer. Others in the series are (318) and (320).**

A failure diameter reduction of 43% occurs when one DETA molecule is added to 5500 molecules of NM. Previous work is reviewed which indicates that sensitization occurs because in basic solutions, the formation of the molecular isomer, the aci-form of NM is favored. NM is H_3C-NO_2; aci-form is $H_2C-NO-OH$. DETA is an amine (diethylene triamine).

320

"Effect of the Number Density of Heterogeneities on the Critical Diameter of Condensed Explosives," Ray Engelke (LANL), Physics of Fluids, 26, (9), pp 2420-2424, September 1983.

Reductions of over 40% in critical diameter were achieved by adding a chemical inert material to NM. The distance between heterogeneities is an important parameter in the production of a critical diameter reduction. For shock wave initiation by a sustained shock wave, even one heterogeneity can enhance the chemical heat release to cause initiation, because in the run-up process, the released energy can support the acceleration of the shock. Release waves that terminate the support, alter the run-up process. Mentions references in which it was found that 150 μm heterogeneities, separated by 200 μm, reduced the initiation (run-up) distance by 15% (312).

JH: This paper again indicates that inert energy concentrators must be considered as well as gas bubble adiabatic compression and chemical sensitizers. This paper is one of a series. See (318) and (319).

321/416

"Shock Initiation of Nitromethane," F. E. Walker, R. J. Wasley (LLNL), UCRL-71696 preprint, Astonautic Acta, 15, 427, 1970.

Proposes that in both homogeneous and heterogeneous initiation, Arrhenius kinetics are not applicable at 60 Kbar and that there enters a "shock-induced non-equilibrium temperature in a shock front that causes a higher-than-equilbrium reaction rate in and near the shock front." Figure 1 shows the interrelation of pressure and duration for NM shock initiation comparing curve with experimental points, and includes points at 6 and 10 Kbar.

JH: This data ultimately led to the $\dfrac{p^2 t}{\rho_0 U}$ shock initiation criterion rather than the explanation offered here. The data points for 6 and 10 Kbar are NOT otherwise available, as this was given to authors as a private communication. The points in Figure 1 could be used to derive the criterion value and extend it to lower pressures. However, later and more complete data is available (322).

Shock initiation at Kbar levels is significant for TEXS with respect to vulnerability to enemy attack, particularly in drums.

322

"Initiation of Nitromethane with Relatively Long-Duration Low-Amplitude Shock Waves," F. E. Walker and R. J. Wasley (LLNL), Combustion and Flame, 15, pp 233-246, 197C.

Reviews, with reference citations, conflicting views on shock initiation of NM. Has time to detonation for 65, 62, and 60 Kbar as 10, 16, 20 μsec with no detonation for 54 and 51 Kbar. (A gas chromotographic analysis of NM showed percent by weight NM 96.4, nitroethane 1.1, nitropropane 2.4, and water 0.1. Specific gravity 1.13 g/cm^3.) Data taken suggests that "energy was liberated near the shock front." Therefore, one has a combination of homogeneous and heterogeneous mechanisms. Denies tiny bubbles by: "Consideration of Henry's law suggests that the surface tension pressure on bubbles with a radius of 10^{-4} cm or smaller would force the gases into solution." Ascribes results to "effective temperatures higher than the equilibrium values behind the shock front," but presents no proof. Compared Arrhenius decomposition to

critical energy fluence $E_c = \dfrac{p^2 t}{\rho_0 U}$ and concludes that latter fits, and that

~60 Kbar experimental results are several orders of magnitude lower than the value calculated from the generally accepted thermodynamic properties of NM in an Arrhenius equation. **JH: No info as to what to use for adiabatic compression at water-hammer pressures. See (323).**

323

"Initiation Patterns Produced in Explosives by Low Pressure, Long-Duration Shock Waves," F. E. Walker and R. J. Wasley (LLNL), Combustion and Flame, 22, 1, pp 53-58, 1974.

Measured shock pressure versus time in NM. The overall average pressure at the shock front for 40 μsec of travel is about 40 Kbar. Curve is given as Figure 5. Suggestion is that there was a peak value of 65 Kbar after about 12 μsec and then dropped to nearly 25 Kbar at about 40 μsec. A sequence of six pic$^+$'s from a framing camera are shown. There appears to be a random patter ' sites at which reaction has started behind the shock front, about 30 μse after the shock has entered the NM. Some process has produced these energy release concentrations so that heat produced from hydrodynamic compression in the NM is not the only source. **JH: The essence is that the sites are not uniformly distributed, so some local energy concentrators are active. Their density and interaction increase with strength of shock.** If the explosive is kept under compression for a period long enough

to provide the critical energy fluence $\dfrac{p^2 t}{\rho_0 U}$, the activated molecules

release sufficient energy to sustain an expanding decomposition reaction. **JH: Results correspond to critical energy fluence. See (322).**

324

"Comments on Initiation Studies," F. E. Walker (LLNL), Sixth Symposium (International) on Detonation, 1976. Unpublished oral presentation—copy as personal communication.

This communication should be considered an extension of the 1974 paper in Combustion and Flame (323). Provides film sequence to show that, in shock initiation of NM as a homogeneous liquid, the detonation originates at or very near the shock front (the inhomogeneous mechanism). He dismisses bubbles and proposes that the initiation process consists of three main effects: "(1) the acceleration and shear forces in a shock wave produce free radicals, atoms and ions very near the front in a process random in space and time that is not necessarily in thermal equilibrium; (2) the free radicals, atoms and ions form initiation sites, again distributed randomly in space and time, at the points where their concentrations are high enough to support expanding exotherm reaction, and the number of sites is a function of the initiating shock pressure; and (3) there is a specific critical energy fluence curve over a wide range of initiating shock pressure for each specific explosive that determines whether or not explosive reaction will occur." **JH: As to 1, the nature of the energy concentrators is speculative. As to 3, later work showed that the critical energy fluence held only for particular explosives, and only for narrow ranges in the p-t plots. For NM see (347).**

325

"Acceleration of Thin Flyers by Exploding Metal Foils: Application to Initiation Studies," R. C. Weingart, R. S. Lee, R. K. Jackson, and N. L. Parker (LLNL), Sixth Symposium (International) on Detonation, pp 653-663, 1976.

Uses thin flyers driven by exploding foils to do initiation experiments including NM. Provides complete analysis of technique. **JH: But not useful for TEXS.** Impact pressures of 9 GPa (90 Kbar) initiated NM, but the initiation was very ragged. Thirteen GPa was definite. Therefore, the threshold for homogeneous NM is around 90 Kbar which agrees with other investigators. The flyer was 0.25 mm thick and diameter of barrel 25.4 mm. Therefore, this threshold is for a very short pulse impacting over a representative area. Flyer velocity of 4 Km/s produced 13 GPa in NM.

326

"Thermal Decomposition of High Explosives at Static Pressures of 10-50 Kilobars," E. L. Lee, R. H. Sanborn, and H. D. Stromberg (LLNL), Fifth Symposium (International) on Detonation, pp 332-337, 1970.

Studied TNT, PETN, HMX, 2,2-dinitropropane, and NM to determine decomposition kinetics versus static pressures. For all but NM, an increase in static pressure decreases the reaction rate (suppression of gaseous interme-

diates). For NM there is an increase of rate of decomposition for a change in static pressure from 10 Kbar to 50 Kbar. However, on a plot of reciprocal temperature versus time to explosion for each pressure, the slope is the same. This implies that the activation energy and, therefore, the reaction mechanism may very well be unaffected by pressure. The effect of rate-increase with pressure is hypothesized as due to the formation of larger concentrations of the rate controlling species. This is proposed as the aciform of nitromethane.

$$
\underline{\text{NORMAL}} \quad H_3C - NO_2 \qquad \underline{\text{ACI}} \quad H_2\text{-}C = N \overset{- \ OH}{\underset{- \ O}{}}
$$

NORMAL $H_3C - NO_2$ ACI $H_2\text{-}C = N$ but this was not proven by measurements done.

JH: The importance is that it suggests that first order kinetics for decomposition (at least at 10 Kbar) cannot be used to include reaction in initiation calculations. Ten Kbar data does not allow a conclusion for adiabatic compression at lower pressures; but possible presence of another mechanism as bubble collapses is disturbing.

327

"Investigation of the Shock Initiation of Liquid Nitromethane," D. R. Hardesty (Sandia), *Combustion and Flame*, 27, No. 2, pp 229-251, October 1976.

Experiments in range 75 to 95 Kbar and 900 to 1100 K in NM by shock. Results support thermal ignition model. Kinetic parameters in a first order overall rate for the initiation-decomposition reaction in NM were obtained giving a rate constant $k_1 = 2.6 \times 10^9 \exp (2300/RT) \sec^{-1}$. k_1 is appreciably different from the rate constant for the unimolecular bond-scissor reaction. The difference suggests that radical reactions influence the overall initiation reaction in liquid NM.

JH: Note that the kinetic path and rate for shock initiation in the range do not indicate rates for the much lower pressures of a water-hammer source. For shock initiation, this paper represents a full review with references and authoritative data for homogeneous initiation.

328

"Detonation Reaction Time in Nitromethane," H. Dean Mallory (NWC), *Physics of Fluids*, 19, (9), pp 1329-1331, September 1976.

The reaction (detonation) zone appears to be the same length for experiments on run-up to detonation for length to diameter ratios of 0.55 to 13.33 for undiluted NM. The run-up for initiating pressures less than the Chapman-Jouguet (detonation) pressure "will arise at first in the shock compressed substance, then overtaking the initiating wave front and cause overdrive detonation of the initial explosive (homogeneous mechanism)."

Measured the reaction time in NM as 22 ± 3 nanoseconds (to Chapman-Jouguet plane) and explained results of experiments (here and elsewhere) in terms of overdrive. The results support the Chapman-Jouguet theory as historically stated.

JH: This result shows how very thin the detonation zone for HVD is by multiplying detonation velocity by reaction time. Using D = 6320 m/sec = 6.32 mm/μsec = 0.00632 mm/nanosec, then thickness CJ = 0.00632 x 22 = 0.14 mm. Note this is NOT the reaction time to be used for low velocity detonation (LVD) where the mechanism is different and the detonation zone is very much larger.

329

"An Equation of State and Derived Shock Initiation Criticality Conditions for Liquid Explosives," Julius W. Enig and Francis J. Petrone (NSWC), Fourth Detonation Symposium (has comments). Paper published in Physics of Fluids, 9, 398, 1966.

Reviews with reference citations shock intiation of homogeneous explosives. Asserts that Mader used an "inadequate temperature equation of state for the unreacted explosive." For NM with bubbles, it is asserted that Mader's (316) model agreed with results because it "depended, in part, on an aribtrary choice of the initial hot spot pressure." In both cases it is believed by authors that correct result will be obtained if an accurate equation of state is used. An E, P, V equation of state is derived for unreacted NM. The input and derived parameters for NM are in Table I (below). An equation of state is proposed for the reaction products based on gamma as a function of detonation velocity, which is considered sufficiently accurate for the initiation problem. Concludes that for homogeneous case, has succeeded with new equation of state that has accurate shock temperature to predict shock initiation. Also asserts that "by approximating hot spot volume by the original void volume and averaging the hot spot energy density increase to give an increase twice that of the shocked explosive—critical hot spot sizes" agree with experiment. Gives the experimental critical hot spot diameter sizes for an 80 Kbar shock as 0.04 to 0.07 cm, i.e., larger would lead to initiation. Gives equations, and Figure 10 below shows dependence on shock pressure.

Table I. Input and derived parameters for nitromethane and liquid TNT. $c_{v,0}$, E_0, Q_0, and β are derived values.[a]

	Nitromethane	Liquid TNT
ϵ	1.637[u]	1.571[b]
$c^*{}_0$(km/sec)	1.647[u]	2.145[b]
$c_{p,0}$(cal/g·deg)	0.4153[c]	0.383[d]
$c_{v,0}$(cal/g·deg)	0.2416	0.1807
$c_0{}^{u}$(cal/g·deg)	0.556[e]	0.500[e]
D_0(km/sec)	6.29[f]	6.633[c]
D_{cm}(km/sec)	10.22[e]	11.00[e]
E_0(kcal/g)	1.273	0.7897
E^*(kcal/mole)	53.6[h]	34.4[i]
X(deg^{-0})	3.9735 × 10^{-3}	
P_0(kbar)	0	0
P_{C_J}(a)	141[j]	171.8[k]
Q_0(kcal/g)	1.113	0.6127
T_0(°K)	300	354
T_5(°K)	436.39	
V_0(cm^3/g)	0.8861	0.679[b]
V_{cm}(cm^3/g)	0.5451[m]	0.4452[m]
Z(sec^{-1})	3.98 × 10^{11}[h]	2.512 × 10^{11}[i]
α_0(deg^{-1})	0.001239[u]	0.00105[i]
β(kbar)	15.83	22.49

[a] See Table II for other derived values.
[b] From a least-square fit of the experimental, U_{cm} data of W. B. Gara J. Chem. Phys. 30, 819 (1959). Experiments are for $T_0 = 354°K$ and $V_0 = 0.679$ cm^3/g.
[c] W. M. Jones and W. F. Giauque, J. Am. Chem. Soc. 69, 983 (1947).
[d] A slight extrapolation of the experimental values of c_p for solid TNT at 1 bar listed by W. R. Tomlinson, Jr., and O. K. Sheffield, Picatinny Arsenal Technical Report No. 1740, Revision 1 (1958), p. 219.
[e] From an equilibrium calculation of the products at the Chapman-Jouguet plane by C. L. Mader (see footnote 7 in Ref. 4).
[f] Reported by C. L. Mader, Los Alamos Scientific Laboratory Report No. LA-2613 (1961), Table II, as due to W. C. Davis.
[g] Due to L. B. Seely, Jr.; see footnote 7 in Ref. b.
[h] T. L. Cottrell, T. E. Graham, and T. Y. Reid, Trans. Faraday Soc. 47, 584 (1951).
[i] A. T. R. Robertson, Trans. Faraday Soc. 44, 977 (1948).
[j] B. O. Craig, in Tenth Symposium (International) on Combustion (The Combustion Institute, Pittsburgh, Pennsylvania, 1965), p. 863.
[k] Value for $V_0 = 0.6873$ cm^3/g and $T_0 = 354°K$; W. B. Garn, J. Chem. Phys. 32, 653 (1960).
[l] Value derived from different measured V_0, T_0 values given in Refs. b and h.
[m] Shock volumes from Eq. (4) for $P_{s} = 86$ and 125 kbar for nitromethane and liquid TNT, respectively; see Table VI in Ref. 6.
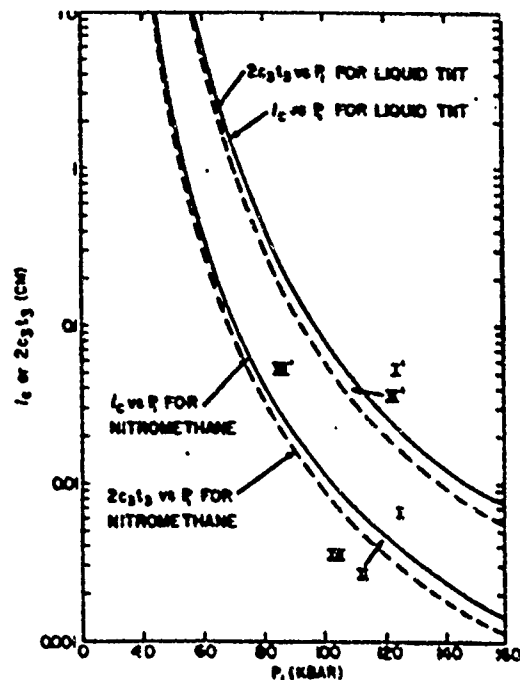

Fig. 10. l_c and $2c_3l_3$ vs P_1 curves for nitromethane and liquid TNT. I denotes the region of super-critical states for nitromethane; II denotes the region in which the nitromethane hot spot explodes but the bulk nitromethane does not initiate; and III denotes the region in which no part of the nitromethane hot spot explodes because the reaction is quenched by rarefaction waves. I and II are regions of subcritical states for the bulk nitromethane. I', II', and III' are the corresponding regions for liquid TNT.

"Effects of Precompression Upon the Detonation Properties of Liquid and Solid Explosives," W. H. Anderson, L. Zernow, A. L. Mottet, Jr., and R. R. Randall (Shock Hydro), Fifth Symposium (International) on Detonation, pp 67-75, 1970.

Hydrostatic pressures up to 90,000 psi were applied to NM increasing the charge density. (NM was sensitized with 5% benzylamine by volume.) The compressibility was estimated theoretically by two different thermodynamical

expressions $\beta = \dfrac{TV\alpha^2}{c_p - c_v} \approx \dfrac{TV\alpha}{\Delta H_v - RT}$. Used $\alpha = 1.239 \times 10^{-3}$ K, $\Delta H_v = 9100$ cal/mol,

$c_p = 0.415$ cal/gm K, $c_v = 0.242$, obtained $\beta = 5.76 \times 10^{-11}$ cm²/dyne for pure NM at 90°F. The corrected ambient charge density of NM at 90°F was 1.114 gm/cc. Found a linear relation of detonation velocity with charge density. Quotes LANL equation D = 6198 - 2855 (ρ_o - 1.114) as standard (JH: Latter equation is preferable to that of this paper) and compares results of this paper thereto (Figure 2).

331/417

"Shock Initiation of Nitromethane, Methyl Nitrite and Some Bis Difluoramino Alkanes," J. G. Berke, R. Shaw, and D. Tegg (SRI), Fifth Symposium (International) on Detonation, pp 237-245, 1970.

NM is CH_3NO_2; methyl nitrite is CH_3O-NO. The CH_3O-NO bond strength is more than 20 Kcal/mole weaker than the CH_3 - NO_2 bond. For constant shock pressure, the reaction time for liquid methyl nitrite is significantly less than the reaction time for NM. In all cases, the reaction times decreased as the initiating shock pressure increased in the range 70 to 130 Kbar. At 86 Kbar the reaction time was found to be 0.7 μsec whereas LANL found 2.26 μsec. Reducing the impurities in NM from around 3% to less than 0.5% had no effect on the reaction time. All of the results can be explained in terms of homogeneous thermal explosion theory. For NM, preshock temperatures of 16 to 40°C were used. Other data extends range to 5°C. Figure 6 gives reaction times versus peak pressures for 5°C and 40°C. At the higher temperatures, the reaction times were lower at the same shock pressure. Failure to propagate occurs at 76 Kbar at 40°C and at 81 Kbar at 5°C. Shock sensitivity to initiation reduces with decrease in temperature. JH: TEXS application regarding initiation of NM at cold T by extrapolation.

332/8

"Investigation of Low-Velocity Detonation Phenomena in Liquid Propellants, Fuels and Explosives," D. C. Wooten, M. Cowperthwaite, and D. C. Erlich, SRI Final Report, June 30, 1972, SRI Project SCU-7771. (Includes "Collapse of a Vapor Bubble Leading to Hot-Spot Initiation," David C. Wooten, March 1972.)

Hot spot initiation by a bubble due to both shock focusing and micro-jetting are generally of interest for shock strength in excess of 50 KBar. Low velocity detonation associated with cavitation model. [See BuMines (13) - (16).] Includes the effects of both heat and mass transfer (vaporization) at the bubble wall. Assumes no viscosity for liquid, temperature equalization, uniform interior, spherical bubble, stationary bubble, incompressible liquid. Sets up and solves the equations. **JH: He does the problem for the simplifying assumptions which are NOT the true case. The value of the paper is the excellent review of the subject to date with 27 reference citations and some techniques used, such as the dimensionless variables chosen. Experiments are clearly required to support or refute theories.**

333

"Detonation Failure Diameter Studies of Four Liquid Nitroalkanes," C. M. Tarver, R. Shaw, M. Cowperthwaite (SRI), Jl Chem Phys, 64, (6), pp 2665-2673, 15 March 1976.

From Table X: Failure diameter calculations are compared with experimental value for homogeneous NM liquid. Values given are $p_0 = 1.127$, $D_0 = 6.285$ mm/μs, $v = 3.881$ mm/μs, $\gamma = 2.53$, $p_{CJ} = 126.1$ Kbar, $\tau_3 = 0.1377$ μs. Calculated failure diameter = 14.05 mm   Experimental = 16.85 ± 2.6 mm.

JH: It follows that for a failure diameter of about ¼ inch, the NM in the pipe (TEXS) will not fail to propagate since the likelihood of the diameter being reduced to this failure diameter is exceedingly small.

334/37

"Ignition and Pressurization of Bubble Regions in Energetic Liquids," Dennis J. Caldwell (Hercules - Utah), 21st JANNAF Combustion Meeting, Laurel ,MD, October 1-4, 1984, Vol II, pp 501-513.

"Jarring a liquid can first cause cavitation followed by pressure pulses strong enough to ignite the bubbles by compression heating. This aggregate will rapidly pressurize, leading to a strong deflagration or detonation event, depending upon external conditions. When the liquid is inhomogeneous, initiation thresholds can be an order of magnitude lower (than for homogeneous)." Bubbles can focus energy into small regions, which reach higher than average temperatures.

Extends the model of Hay and Watson [6th Detonation Symposium (13)] for a system of burning bubbles in order to incorporate viscosity. **JH: Still saddled with incompressible fluid and linear burn rate.**

335

Reserved for future use. Paper is in preparation.

336/53/641

"Investigation of Detonations in Liquid Hydrazines," H. Beeson and M. Plaster, 1988 JANNAF Safety and Environmental Protection Subcommittee Meeting, Chemical Propulsion Information Agency, May 1988.

Provides a background with references on shock initiation of detonation, low velocity detonation and the role of "hot spots" or energy intensifiers in these processes. Quotes Watson that LVD requires higher sound velocity in wall of container than in liquid and wall thickness above a minimum value. Describes a modified card-gap apparatus with a 2 inch diameter.

Hydrazine did not detonate with a donor charge of 0.49 lb of C-4. Damage consistent with an LVD in 0.5 inch tubes with 0.035 inch wall thickness was not observed (latter is below the 0.06 Watson criterion).

Experimental results indicate that the explosive events observed in rapid compression experiments by Baker (52) involve more complex phenomena than simple shock initiations. **JH: Baker stresses froth compression as key mechanism and considers physical kinetics of froth as control mechanism.**

337

"The Effect of Energy Release on the Regularity of Detonation Cells in Liquid Nitromethane," R. Guirguis, E. S. Oran, and K. Karlasanath, 21st Symposium (International) on Combustion, pp 1659-1668, 1986.

Chemical decomposition of NM is described by a two step model composed of an induction time followed by energy release. Used time dependent two dimensional simulation to study effect of energy release. Simulations show energy release process controls whether the detonation does become one dimensional or becomes multidimensional (cellular). **JH: Here the dominant parameter for homogeneous NM is taken as the chemical kinetics of decomposition, but preceded by an induction time. One may regard the induction time as associated with random distributions and their number density of ignition sites as proposed by Walker (LLNL) (323). The growth at sites and their interaction leads to cellular structure. For the heterogeneous NM, one superimposes energy concentrations whether gaseous or solid "bubbles that establish a region when reaction is greatest, namely close to the shock front**

which ignites these energy concentrators." Depending on heterogeneity one can have any state between the two extremes. This is sometimes stated as a combination of physical and chemical kinetics, where the former sets the T and p in which the latter starts/acts.

338 - 340

Reserved for future use.

341/12

"The Initiation and Growth of Explosion in Liquids," G. D. Coley and J. E. Field, 9th International Congress on High Speed Photography, August 2-7, 1970, Denver, Proceedings SMPTE, pp 466-473.

The transition from deflagration to a low velocity detonation was found to depend on the production and collapse of cavities in the liquid ahead of the reaction front. **JH: Note that if liquid has the distributed bubbles due to another cause, e.g., previous cavitation, then ignition at one site would rapidly lead to low velocity detonation.** Reviews work of authors pertinent to role of cavities. Photographed the role of cavities interacting with a deflagration front. A cavitation front first creates the bubbles and then the deflagration front moves in and a transition in velocity of propagation follows. Used primarily nitroglycerin. The transition depends on the adiabatic collapse of bubbles in the liquid ahead of the reaction front. **JH: The energy intensifier profile is the determining factor on the transition from deflagration to detonation; it also applies for LVD to HVD transition.**

342/418

"Shock Induced Reaction in Explosives and Propellants," R. Merrifield (ERDE, GB), AD 752372, 24 pages, 1972.

The modified gap test was used to determine the threshold for burning which for long duration lower pressures was found to be much lower than for initiation of detonation. The Hugoniot "adiabat" for NM is given as $U = 1.56 + 1.96\,u$ where U is shock velocity and u is particle velocity, both in mm/μsec. Figure 15 compares results for different sources. The threshold pressure for detonation is given as 104 Kbar for NM which is higher than the usual ~85 Kbar value. This is attributed to the possible difference in purity of the samples. "The particular NM sample used here was part of an old consignment originally intended for use as a fuel. It is probably typical of the quality of NM samples which might be handled or stored in bulk.

JH: This raises the question of whether old NM might be more difficult to initiate. This effect would be accentuated at the low temperature extreme. A threshold pressure for burning was not found for NM. The axial velocity of the material blow-off after 50 mm of travel (U_a) was obtained. Figure 5 shows U_a versus P_g (pressure incident) for NM as a smooth curve until 109 Kbar where detonation leads to a sharp discontinuity. Therefore, there is no particular threshold for a self-propagating detonation, but increasing reaction responds to increasing incident pressure. JH: With energy intensifiers, there may be a threshold for burning followed by run-up to LVD.

343/23

"Role of Cavities in the Initiation and Growth of Explosion in Liquids," G. D. Coley and J. E. Field (Cambridge, GB), Proc Roy Soc (London), Ser A, 335, 1600, pp 67-86, 1973.

This paper provides extensive results and understanding on how bubbles and the stimulus profile together determine the ignition, consequent deflagration, and low velocity detonation in the liquid. In particular, the role of confinement and release waves from the liquid interface therewith is treated. The interaction of bubbles is significant as reaction in one bubble generates a flow into adjacent bubbles. Jetting in later stages is important. Cavity collapse must be rapid so that heat losses do not prevent adequate temperature rise for initiation, and the environment must last long enough for initiation to occur. Some decomposition can occur followed by quenching of further growth reaction.

344/419

"Low Order Reactions in Shocked Explosives," Neill Griffiths and V. C. Broom (RARDE, GB), Fourth Symposium (International on Detonation, pp 462-472, 1967.

When a homogeneous or heterogeneous explosive is shocked, the energy can be released either rapidly or slowly depending on the explosive properties and intensifiers and on the intensity of the shock. If sufficient energy is contributed to the shock front it will accelerate, or if energy in the rear is sufficient it will overtake the shock—in both cases and for combinations, detonation can be achieved. . If insufficient energy is contributed, the shock will decay. The cavitation depends on the duration of the shock wave. "If the pulse length is gradually increased, a balance can eventually be obtained between energy lost and energy produced and a pseudo-stable detonation is set up." The critical pulse length is related to the reaction zone length in the propagation of detonation. An intense but sufficiently short shock pulse may not lead to initiation. JH: The initiating system for TEXS, in order to be positive and reproducible, must have a pulse length at least a multiple of the induction time and over a volume a multiple of failure dimensions.

345

"Dependence of the Velocity of Detonation of Nitromethane on Its Initial Temperature," M. P. Murgai (India), Jl Appl Phys, 28, 745, 1957.

Calculates using covolume $\alpha = 0.5407$ cc/g, coefficient of cubial expansion $\beta = 1.1638 \times 10^{-3}$ $(°C)^{-1}$ and $\rho_o = 1.128$ all for 25-30°C and a formula for the detonation velocity, that $dD/dT_o = -4.5$ m/sec °C. For example, detonation velocity decreases with temperature, attributable to density decrease with temperature. In an early reference (310) LANL authors gave -3.7 m/sec °C as the combined effect of density decrease with increase in temperature and a general increase of detonation velocity with increase in temperature.

JH: Using -4 m/sec °C and a +75°C change, the change in D would be a -300 m/sec for approximately the range of TEXS. For D $\approx$ 6000 m/sec, this is a 5% decrease from upper to lower T limit. However, cratering depends on pressure (which is proportional to D^2) and initial density of the explosive, so that the decrease in cratering will be over 10% for the range of TEXS.

346

"Detonation of Nitromethane," G. Nahmani and Y. Manheimer (Israel), Jl Chem Phys, 24, (1), pp 1074-1077, May 1956.

Calculates for the detonation of homogeneous NM, D = 6060 m/sec, p = 89,000 atmospheres, T_{cj} = 4000 K, and specific volume = 0.69 cm^3/g. JH: This was done in 1956. Today more accurate results are immediately obtained with the TIGER computer program or even with the simple to use Kamlet formulas. He finds a critical diameter of 27 mm, a length of reaction zone of 0.3 to 0.6 mm, and reaction time of $0.6 - 1.0 \times 10^{-7}$ sec.

JH: See (328) for more recent values. Zone is 0.14 mm thick; reaction time = 0.22×10^{-7} sec. See (333) for more recent value of critical diameter = 14.05 mm calculated, 16.85 experimental.

347

"Shock Sensitivity of Nitromethane with Well Defined Hot Spots Distribution," C. Fauquignon and H. Moulard, French German Research Institute of Saint-Louis, ISL-CO 217/77, Act Astron, 5, pp 1035-1040, 1978.

For heterogeneous NM, the controlling temperatures are those of hot spots which cannot be calculated with reasonable accuracy. For homogeneous NM, finds that shock sensitivity can be well predicted by a thermal explosion model in which the induction time is calculated by integrating the Arrhenius formula with an equation of state appropriate for T and p. Figure 1 shows agreement between theory and experiment for homogeneous NM. To study heterogeneous, set up NM with a known distribution of hot spots created by impacting a base plate with holes 2.5 mm i.d. and 1.5 mm depth. The spatial distribution is varied. Streak camera records events following impact of flyer

plate. For a given hot spot, the leading parameter is the distance between hot spots. Successive interactions are followed. Figure 4 compares homogeneous NM and heterogeneous model results.

JH: This paper verifies that the key parameters are the strength of the hot spots and the cooperative action between them, which depends on their spacing. One can imagine a distribution in intensity and spatiality as determining the course of events. But since the distributions are not normally known, measurements must be made for the real or accurately simulated situation.

348

"Characterization of an Overdriven Detonation State in Nitromethane," L. Hamada, H. N. Presles, C. Brochet, and R. Bouriannes (Poitiers), and R. Cheret (CEA), "Dynamics of Shock Waves Explosions and Detonations," paper presented at Ninth International Colloquium on Gasdynamics of Explosions and Reactive Systems, Poitiers, France, July 1983, published by AIAA, pp 343-349 of Vol 94 Progress in Astronautics and Aeronautics.

Overdriven states of detonation are created in NM by geometry producing a Mach stem. The overdriven pressure is 35.5 GPa (355 Kbar) and the detonation velocity ~8 mm/μsec. The brightness temperature of the overdriven state is 900 K higher than the CJ state. Quotes relation for constant γ along Hugoniot of detonation products for detonation velocity of overdriven state (using Ideal Gas EOS) which is adequate for an estimate

$$(D/D_{CJ})^2 = (Z^2/2Z) - 1 \text{ where } Z = p/p_{CJ}.$$

JH: Nowadays, one would derive the Hugoniot curve by TIGER or measure it and draw a Rayleigh line tangent to overdriven state to get corresponding values of D and p. This would avoid assumptions of ideal gas and constant γ which are only approximations at best.

349 and 350

Reserved for future use.

351/56/643

"On the Low-Velocity Detonation of Nitromethane," A. A. Schilperoord (Netherlands), Seventh Symposium (International) on Detonation, pp 575-582, 1981.

Experimental work is described which shows that nitromethane is able to undergo a low-velocity detonation (LVD) reaction, if confined in a steel tube

and subjected to a shock wave of appropriate strength. It is concluded that the occurrence of LVD in nitromethane requires such conditions as to enable both cavitation of liquid and sufficient explosive reaction. The latter condition means a rather strong confinement, because of the relatively low reaction rate of nitromethane. The results of this work may lead to an improved design of a gap test for the investigation of the shock wave sensitivity of liquids.

A stable LVD is characterized by a constant velocity higher than the sound velocity of the cavitated liquid.

Results explained by Watson theory. For NM, when sufficient confinement is available, its sensitivity is comparable to that of sensitive high explosives (~10 Kbars). **JH: Data is needed for the TEXS configuration; pipe not enclosed and also buried; and versus temperature.**

Dimensions of Steel Tubes with Identification (in mm)

Inner diameter	30	31	31	50	31.5
Outer diameter	35	38	51	70	63.5
Wall thickness	2.5	3.5	10	10	16
Length	750	750	750	750	750
Identification	30/35	31/38	31/51	50/70	31.5/63.5

LVD in 31.5/63 steel tube; marginal in 50/70 and 31/51 which have same wall thickness.

352/55/642

"Sensitivity of Nitromethane for Low Velocity Detonation," R. R. Ljsselstein (Neth), Propellants, Explosives, Pyrotechnics, 10, 1, pp 14-17, February 1985.

Maps the shock loading regime in which a stable LVD can develop using a modified gap test (details given). Including LVD's, NM appears to have a sensitivity comparable to that of relatively sensitive high explosives. Explanation is that of Watson, with cavitation precursor. Threshold for heavily confined NM with a hollow axial tube for LVD is 1.5 GPa (15 Kbar, 15,000 atm), HVD is 7 GPa. The threshold and violence of an LVD explosion are strongly influenced by the dimensions, materials of the confinements, and presence of axial inclusions. ". . . under confined circumstances such as may occur for instance when it is pumped through pipelines nitromethane should be treated as a reasonably sensitive high explosive." JH: The data in this paper are not for the conditions encountered in pumping through pipelines. The threshold for LVD far exceeds any water-hammer generated pressure. Data may have value for fragment/plate impact or sympathetic detonation and for propagation of LVD instead of HVD regarding performance.

Found the distance required to establish an LVD for the strong confinement used here (steel tube i.d. = 31.5 mm, o.d. = 63.5 mm) was 150 to 250 mm which means that test set-up requires a very long tube (NOL large scale gap

test is only 140 mm) or erroneous results may be inferred. The shock velocity of the stimulus may decrease to the sound velocity level before building up to the LVD value (1200 m/s).)

The possibility that the initiation scheme in TEXS will produce LVD instead of HVD, greatly impairing performance, requires serious consideration.

353/646

"Reaction Zone Measurements in High Explosive Detonation Waves by Means of Shock-Induced Polarization," R. R. Ljsselstein (Netherlands), Combustion and Flame, 66, pp 27-35, 1986.

NM was contained in a 100 mm long 28 mm inner diameter PVC tube. Uses shock induced polarization in confinement to monitor propagation and deduce reaction time and, therefore, reaction zone length. For NM at density 1.13 g/cm^3, reaction time is 27 nanoseconds and reaction zone length is 0.12 mm. JH: See 328, 333, and 346.

354

"A Model for the Initiation of Explosives—High and Low Velocity Detonation," C. O. Leiber (Germany), Jl of the Industrial Explosives Society, JAPAN Vol 34, No. 4, pp 200-207, 1973.

This work tries to take into consideration the motion of the bubbles with respect to the fluid. The entrainment depends on the viscosity described by the "Roth number" representing the fraction of the energy of acceleration to viscous dissipation of the discontinuity in the matrix. A discontinuity bubble has no relative motion to the fluid if viscous forces are dominant. If inertial forces dominate, the bubble can move up to three times the particle velocity. A shock attack provides both inertia and viscosity to the medium in the shock thickness, which is finite. A bubble may have an infinite duration in the shock wave. In this case or for close support, energy is fed directly to the shock and the shock steepens. Asserts that cavity formation is occurring in the shock thickness in a size appropraite to pressure and calculates radius. For NM from 75 Kbar and up, 2 microns is proposed. For NM in pure state, asserts that only HVD is possible and that at a detontion velocity of 8 mm/μsec (8000 m/s), the velocity of fully actuated pores reaches 9600 m/s. JH: This is the only study I have seen on entrainment of bubbles. I don't believe this was used by PCRL in their full adiabatic compression theory of shock initiation.

355

"Shock Augmentation by Bubble Flow," C. O. Leiber (Germany), Jl Appl Phys, 47, (9), pp 3971-3978, 1976.

This paper is a follow-up to a previous one by the same author (354). He substantiates his earlier argument that the bubble transport and evolution in the flow must be included for a complete treatment of low velocity detonation.

Available also in the paper are the shock Hugoniot for NM for ρ_0 = 1.125 and $U = A + Bu$ where $A = 1.560$ mm/μsec and $B = 1.721$ (from Thiel (LLNL) compilation).

JH: This is an interesting paper for the theoretical side of LVD, but not necessary to those concerned with TEXS problems.

356

"The Structure of Detonation Within the Bubble Dynamic Model," C. O. Leiber (Germany), Shock Waves in Condensed Matter, Paris, pp 183-194, 1978.

Recognizes the fact that initiating detonation depends on the number and spacings of bubbles and their diameter; but adds the important feature of the phase of response between the bubbles. His calculations show that the maximum response occurs when the bubbles are approximately in phase. However, phases within 150° (0° identical, 360° identical) lead to a pressure of 60-70% of that with perfect synchronization.

JH: The model is idealized too far from reality. However, the qualitative features are valuable. This is an important attempt to relate the cooperative effect between bubbles to the nature of the bubble profile in the space and time. It is certainly true that this behavior is critical to initiation of detonation, but it is equally the case that there is a manifold of distributions that can lead to detonation—not a unique set of circumstances.

357

"The Measurement of Detonation Temperature of PETN Crystal and Nitromethane," Shi Huiseng, Han Chengbang, and Kang Shufang (China), Combustion and Detonation Phenomena, 19th International Annual Conference, Germany, 1988.

The unstable detonation and fluctuation of detonation temperature of NM were studied. The detonation temperature of NM is about 3600 K. Plastic tubes used were 27, 20, 16, and 9 mm i.d. The smaller diameters had the greatest fluctuation in detonation temperature. Failure occurs at 9 mm. For 20 and 16, only a short distance of propagation occurs. Luminous spots have a temperature of 3800 K. JH: The equipment for two-color pyrometer measurement of temperature is outside scope of interest for TEXS.

358

Reserved for future use.

359

"Effects of Liquid Diluents on Detonation Propagation in Nitromethane," Masao Kusakabe and Shuzo Fujiwara (Japan), Sixth Symposium (International) on Detonation, pp 133-142 (includes discussion), 1976.

Covers, with references, the effect of inert diluents on detonation properties of NM. Figure 2 plots critical diameter versus diluent content in volume percent of acetone, nitroethane, carbon tetrachloride and chloroform. Critical diameter increase with diluent content. Values shown begin with 10%. JH: This data is, therefore, not useful for impurities, e.g., nitroethane. Figure 3 gives detonation velocity versus inverse diameter for NM at 25°C. D = 6.2601 - 0.0405 (1/ϕ) where D is in Km/sec, ϕ charge diameter in cm. Measurements were done in brass tubes. The temperature coefficient is cited from reference (Davis) as dD/dT = -3.9 m/sec/°C. Combining leads to 6343.4 ± 5 at 4°C for infinite diameter which is about 30 m/s lower than direct measurement by Davis. One percent dilution in volume reduces D by about 10 m/sec, therefore, difference attributed to impurities present. JH: This provides means to correct for nitroethane, which acts as an inert diluent in NM. Note all values are for HVD.

360 through 374

Reserved for future use.

375/75

"Effects of Gas and Liquid Properties on Detonation-Wave Parameters in Liquid Bubble Systems," A. V. Pinaev and A. I. Sychev, Combustion, Explosion and Shock Waves, pp 735-742, May 1988.

Optical studies have shown that surfaces are unstable during collapse which can be due to bubble interaction in the wave or instability in the collapse (Taylor). The compression distortions increase as viscosity decreases at higher temperatures, which increases effective surface area, which increases the heat loss from the gas heated by compression and ignition, so detonation velocity is reduced. The temperature rise in the bubbles

falls as viscosity decreases, as the compression differs substantially from adiabatic, depends on the rate of collapse, and the ignition delay increases exponentially and can even prevent ignition. **JH: Note idea that surface breakup works against ignition; but once ignition does occur the high surface area should accelerate growth. Low viscosity is said to be critical to surface breakup and will show up at the higher temperature; its effect is to work against ignition. At the lowest temperature (of liquid) viscosity is high and surface breakup is reduced; but the entire story requires including compressibility which affects rate of collapse. This was not done. Need studies versus temperature for NM (no NM in this study), where all mechanical properties enter simultaneously. This paper based on high detonation velocity as altered by collapse of contained bubbles. Hence it is for LVD. Note that ignition also depends on viscosity which is relevant to hazard. It is not clear at what temperature hazard is greatest, but see (29).**

376/77

"Structure and Properties of Detonation in a Liquid-Gas Bubble System," A. V. Pinaev and A. I. Sychev, Combustion, Explosion and Shock Waves, pp 360-368, November 1986.

These authors have a more recent paper (75)/(375).

The detonation wave propagates by igniting bubbles radiating shock waves into the surrounding liquid which in turn ignites bubbles ahead of the wave. "Generally speaking, bubbles in the liquid have a nonspherical form, but with increase in liquid viscosity they become close to spherical." After ignition, the bubbles expand and radiate a shock wave followed by rarefaction zones in which a large number of fine bubbles are found. **JH: Since viscosity increases at the low temperature extreme, the bubble collapse becomes spherical and rate of temperature rise within depends on compressibility and diffusivity.**

377/78/651

"Detonation Waves in a Liquid-Gas Bubble System," A. I. Sychev, Combustion, Explosion and Shock Waves, pp 365-372, November 1985.

This author is coauthor in two more recent papers (75/375) and (77/376).

Describes equipment for creating a column of liquid containing bubbles and studying shock wave propagation including instrumentation used.

Referring to adiabatic compression by a shock wave, he notes that "if a bubble is not ignited upon compression before formation of a cumulative jet, subsequent ignition of the explosive mixture in the bubble is possible upon propagation of the liquid jet."

Regarding possible bubble interaction, he finds that the region of hot

gas mixture explosion products in the bubbles does not exceed 6 d_o while the mean distance between bubbles in the case photographed was 2.3 d_o. JH: A jet in a bubble occurs when the collapse is due to a planar shock on a spherical bubble. For compression due to slow rise of pressure, a spherical collapse is more likely. With bubble, surface breakup is also a possibility but not formation of a Munroe jet in absence of strong shock.

378/76

"Detonation Transformations in an Aerated Liquid," B. N. Kondrikov, G. D. Kozak, V. B. Oblomskii, and A. V. Savkin, Combustion, Explosion and Shock Waves, pp 195-202, March-April, 1987.

Reader is directed to Summary No. 76/378 in Category 1, Adiabatic Compression.

379

"Chemical Kinetics of Detonation in Some Organic Liquids," B. N. Kondrikov (Soviet), presented at the 8th ICOGER, Minsk, USSR, August 23-26, 1981. Published by AIAA in Vol 87, Progress in Astronautics and Aeronautics, Shock Waves, Explosions and Detonations, pp 426-439.

The failure diameter of NM appeared to be much more sensitive to the additives than the gap test. Just 0.02% di-or triethyamine or pyridine reduces d_f by a factor of 2; 2% reduces it from 13 to 1.5 mm. JH: Dimensions for TEXS exceed the NM failure diameter of about 2 cm, so this is no problem. This paper gives details of failure diameter as a function of concentration of sensitizer for many additives and several energetic liquids. JH: Note that for a field test of change in NM for TEXS, the critical diameter seems a sensitive index.

380

"Detonation of Nitromethane," B. N. Kondrikov, G. D. Kozak, V. M. Raikova, and A. V. Starshinov, Dokl Akad Nauk, SSR, Phys Khim, 233, 402, 1977. Translation

In the presence of acid and bases, NM forms nitronic acid whose chemical stability is much lower than that of initial pure NM. Gives results for many additives and results are complemented by those in later paper by same lead author (379). Regarding TEXS, states, "The effect of water dissolved in NM was found to be quite significant: Addition of 2% water decreased d_c (critical/failure diameter) from 13.5 to 8 mm." JH: This means that the NM became more sensitive; whereas without water, a diameter of at least 13.5 mm was required to propagate detonation. Now only a minimum of 8 mm was required. In general, failure diameter is a much more sensitive indicator to effect of additives than the gap test. Change due to small percentages of water in NM in a hydraulic hammer test would have to be separately deter-

mined for pure NM and with a bubble profile present. Note significance for a TEXS field test for changes in sensitivity of NM based on change in failure diameter.

381/80

"On the Mechanism of the Reaction "Hot Spots" Origin at Liquid Explosives Detonation," A. N. Dremin, V. Yu. Klimenko and I. Yu. Kosireva (USSR), Eighth Symposium (International) on Detonation, pp 678-687, 1985.

Describes an "accumulation" mechanism in which translational modes are excited first, then redistributed to vibrational modes, and if the rate of energy flow into the latter exceeds a relaxation process, energy density rises. But states "the mechanism does not come into action if the molecules are small like NM molecules." Investigates the alternate proposed mechanism that overheated micro-regions due to shock interaction with density discontinuities are source of initiation in wave. Does calculation to show that this interaction leads to magnified regions of high temperature, validating the model. Notes that the whole actuation process will accelerate—if the characteristic time of their development is comparable or smaller than the characteristic life time of the overheated regions. JH: This paper is primarily a Category 3 paper. However, there is an analogy to be drawn regarding adiabatic compression of bubbles. On a larger scale there are macroregions whose role depends on the characteristic time of development exceeding transport of generated energy away from the site (and the energy released by reaction. This highlights the importance of rate of compression.

382/84

"Detonation of the Critical Shock Initiation Conditions for Homogeneous Explosives," I. M. Voskoboinikov, V. M. Bogamolov, and A. Ya. Apin, Combustion, Explosion and Shock Waves, 5, No. 4, p 323, 1969.

Decomposition kinetics must be obtained on the homogeneous liquid which can be done most readily in shock-compression experiments because one can get to the p, v, T state of interest in times in which substance is unable to undergo chemical reaction and create that state over a significant volume. The state is maintained for so short a time that transport can be neglected. JH: For our use the assumption must be made that kinetic pathways and rates so determined can be extrapolated down to adiabatic compression of a bubble over a longer time at much lower pressures. His calculations, "neglect burnup of the explosion during the adiabatic explosion induction period." For liquid NM, the critical pressure for a shock-initiation is 93 Kbar experimentally (ref cited) and author calculates 115 Kbar. The ignition lag is given as 1 microsecond for this shock with temperature rising to 1200 K. JH: Value of ignition lag entirely different for bubble collapse—this is all for homogeneous liquid. Other references go as low as 85 Kbar for shock initiation in homogeneous NM.

"Initiation and Development of Detonation as a Result of the Action of Weak Shock Waves on Liquid Explosives," A. V. Dubovik and V. K. Bobolev, *Combustion, Explosion and Shock Waves*, 5, No. 3, p 245, 1969.

For excitation of explosion by weak shocks (1 - 10 Kbars), shock heating of the liquid is not more than 100°C; gas bubbles, impurity particles must act as "hot spots." Liquids have little resistance to negative stresses and therefore cavitate. This mechanism acts as the propagating factor for low velocity detonation by presence of a precursor wave of cavitation. Precursor can be achieved by sound speed in material of vessel exceeding weak shock velocity on other conditions that create a cavitated state, e.g., barriers, change in direction leading to rarefaction waves. Low velocity detonation could not be initiated in NM using a weak explosive as initiator. If NM is exposed first to a weak (about 1 Kbar) and then a stronger (about 50 Kbar) shock, the liquid does explode. **JH: An initiating system might be designed to do this to assure reproducible initiation of NM in the TEXS application.** NM in a vessel measuring 3.5 x 5 cm and 5 cm tall with thick Plexiglas walls, did not, in homogeneous state, initiate with a 50 Kbar shock. If, however, a metal (or glass) plate is placed a small distance above the NM, the impact of the ejected liquid against this surface leads to explosion. **JH: Another form of energy concentrator.** A layer of NM 25 mm thick was introduced between thick Plexiglas plates to form a charge 50 mm wide and 150 mm thick. Cavitation was produced by exploding a weak charge on top of the NM. The initiating shock generator at the bottom provided 50 Kbar after a delay. Low velocity detonation, or a strong shock wave supported by reaction, was propagated at 2450 m/sec. Near the end of the charge the wave velocity was 1700 m/sec. Attenuation of the reaction wave in NM is attributable to poor support from the interior of the wave, where the slow reaction apparently ceases immediately after penetration of the rarefaction wave into the reaction zone. **JH: Low velocity detonation has a very long detonation zone. Hence geometry effects and confinement can easily alter the velocity of propagation and even lead to quenching if the liquid the wave is entering has reduced cavitation. For adequate diameter confinement and booster, the NM should detonate high order which is essential to achieve the required performance of NM for TEXS.**

"Sensitivity of Some Explosives to Shock Wave," V. S. Ilyuklin and P. F. Pokhil, Dokl. Akad. Nauk., SSSR, 140, pp 179-180, 1961. C.A. 56, 6229h, 1962.

Detonation wave was transmitted through a copper barrier varied from 5 to 30 mm as a type of gap test. For various explosives, Table 1 gives the minimum (critical) pressures in the front of the initiating wave corresponding to maximum delay of detonation. **JH: This data is a point on "Pop plot."** Relative values, those to left of vertical line, have the higher values associated with homogeneous explosives. These relative values can be changed by increases in size of donor and acceptor and confinement (by a factor of about two).

Explosive	HMX	Cast TNT	Liq TNT	NG	NM	Pressed TNT	Pressed HMX
Density (g/cm³)	1.80	1.62	1.46	1.60	1.14	1.63	1.74
P critical (Kbar)	10	11.5	11.0	8.5	9.0	2.2	1.5

Estimated that 0.1 Kbars, the adiabatic compression temperature (ref cited) is 700 - 800°C which evidently is sufficiently high for rapid ignition of the explosive. But 0.01 - 0.02 Kbars corresponds to a temperature rise below 100°C and ignition may only result by presence of energy concentrators (heterogeneous case). **JH: Pressures quoted seem low for shock initiation of high order detonation.**

385

"On the Mechanism of the Reaction "Hot Spots" Origin at Liquid Explosives Detonation," A. N. Dremin, V. Yu. Klimeko, and I. Yu. Kosireva, Eighth Symposium (International) on Detonation, July 15-19, 1985, NSWC MP 86-194, pp 678-687.

JH: This is the current paper of a series in which the "Dremin institute" has worked on liquid explosives. The earlier papers are (386) through (390). The relationship to TEXS is limited to "data-in-passing" and questions of stability of and additives on detonation. Only features somehow related to TEXS are noted here.

The passing shock front changes small density fluctuations into overheated microregions in which the reaction is 5-10 orders of magnitude faster than in the surrounding substance. The spot's further development will correspond to thermal explosion irregularities. Summarizes the development of the three stage mode. **JH: The microregions are not due to bubbles, but are of a smaller dimension due to density nonhomogeneities. However, bubble compression provides macroregions that can be similarly modeled.** In Discussion (page 682), notes larger hot-spots for NM (10^{-7} mm) with temperature $\approx 1300 - 1500$ K versus 1000 K so that reaction proceeds an order of magnitude faster. Decomposition then spreads by chain reaction from hot spots.

386

"Unstable Detonation Front Structure in Liquid Explosives," A. N. Dremin, V. M. Nelin, and V. S. Trofimov, Fiz. Gor i Vzr, 16, 3, pp 316-323 (translation), 1980.

JH: See (385). Degree of detonation front stability is linked to kinetic properties of liquid explosives. This can be understood in terms of an overall Arrhenius law, using two parameters: $\beta = RT_0/E$ and $\gamma = \beta \cdot cT_0/Q$; where E is activation energy, c specific heat, and Q specific isothermal heat of the overall reactions. For $\beta \ll 1$ and $\gamma \ll 1$, normal behavior occurs.

Unstable detonation occurs for $\beta < \beta*$ and $\gamma < \gamma*$ where * denotes critical values.

The possibility of quenching by a rarefaction wave is linked to $dT/dt < 0$. This can be achieved if β, γ drop below critical values and the reaction rate is not sufficiently high to compensate; i.e., self-heating underway can overcome insensitivity due to lack of hot spots (microregions). The theory is explored in detail for NM/Acetone mixtures where acetone presence leads to detonation front inhomogeneities (~2 mm). **JH: The qualitative ideas apply equally well to bubbles as the inhomogeneities.**

387

"Structure of the Detonation Front in Condensed Explosives," A. N. Dremin, O. K. Rozanov, S. D. Savrov, and V. S. Trofimov, Fiz. Gor i Vzr, **5**, 1969. Translation in <u>Combustion, Explosion and Shock Waves</u>, pp 199–207.

JH: See (385). Summarizes the accepted ZND theory of detonation and notes that it is a special case of a description of nonsmooth detonation waves. In the latter theory, at the C-J plane, not only is chemical reaction completed but the dissipation due to turbulence, which also provides heat, is damped. To investigate the nature of the detonation zone it is necessary to investigate the inhomogeneities that are propagated over the surface of the detonation front. Experimentally this was done by using NM/Acetone mixtures to introduce inhomogeneities. Applies the ideas to pulsating detonation and transitions between forms (weak, strong, CJ, LVD, HVD) of detonation. For NM, dilution with acetone, inert additive is analagous to going over to a less powerful explosive with the same initiation energy. This reduces D and T_0 and the ratio T_0^2/Q, which leads to a decrease in β and γ (see 386), which leads to a nonsmooth front, which is verified experimentally. The inhomogeneities determine the detonation limits ($d_{critical}$).

388/86

"Critical Phenomena in the Detonation of Liquid Explosives," A. N. Dremin, Twelfth Symposium (International) on Combustion, 1968.

JH: See (385). It was found (refs cited) that the front of a detonation wave in NM was rough and that the chemical reaction at the detonation front did not occur simultaneously. For some other explosives, e.g., NG and TNM, it is smooth. The ratio for the induction period τ to the overall reaction time Δt representing considerable heat release underlies stability of the detonation front. Thermal theory implies that $\tau/\Delta t$ strongly depends on activation energy, heat of explosion, initial temperature of chemical decomposition with ratio tending to unity as the first two go higher or the last lower. For $\tau/\Delta t \approx 1$ tends to be unstable; if $\tau/\Delta t$ is low, the detonation front tends to be stable. Since charge sizes are finite, limiting initiation conditions depend on $\tau/\Delta t$. Since shock compression of booster will die off, if $\tau/\Delta t$ is large, initiation may not occur or rarefactions will enter before a steady state can be achieved. This determines threshold

for shock initiation. For $\tau/\Delta t$ large, local adiabatic explosions control the frequency of the detonation front pulsations (JH: **Dependence on local sites-heterogeneity**) and the scale of its nonuniformity. For weak explosives with an unstable front of the NM type, breakdown of the reaction occurs at the front of the lateral rarefaction wave.

389

"On the Detonation of Nitromethane," A. N. Dremin, O. K. Rozanov, and V. S. Trofimov (Soviet), Combustion and Flame VII, pp 153-162, 1963.

JH: **See (385).** Considers detonation in NM in light of theory of detonation in gases. Observed bright and dark zones which leads to conclusion that there may be regions of undetonated NM. This can occur in going from one diameter to a larger one so that rarefaction waves are generated (cornerturning). JH: **For TEXS the diameter is far above the critical diameter for NM. Even if an irregularity at a joint allows for a sudden expansion, the rarefied region will participate before the pipe bursts. In fact, surface irregularities generate inhomogeneities that help sustain the propagation by shock interactions.**

390

"The Detonation of Nitromethane Close to the Limit," A. N. Dremin, G. A. Adadurov, and O. K. Rozanov, Dokl, Akad, Nauk, SSR, Phys Khim, 133, pp 771-773, 1960. Translation

JH: **See (385).** In the majority of cases, where boundary effects occur, whether rarefactions or shocks are generated, one can observe light and dark regions in the NM as the detonation progresses. Details of the experimentally observed variations in emission of light are described in detail. [Later papers, e.g. (389) offer an explanation in terms of the role of inhomogeneities in propagation of the detonation.] The NM in the dark region apparently loses its transparency under the action of the shock wave where reaction is not yet present.

JH: **This is the earliest of the Dremin "institute" papers included in the compendium (385) through (390).** It is suggested that the reviews be read starting with (385) before studying any one paper in detail. The application to TEXS is primarily for background.

CATEGORY 4

TEXS PROBLEMS

REFERENCES

400

Reserved for future use.

401

"Proposal for TEXS, Tactical Explosive System, Nitromethane-Based Explosives Subsystem," Prepared by Angus Chemical Company, Report No. ACC-201, July 1988.

402

Reserved for future use.

403/506

"Preliminary Hazard Analysis (PHA) Nitromethane and Ammonium Nitrate Based Tactical Explosive Systems (TEXS)," Billy R. Sharp, SRS Technologies, Draft Technical Report SRS/STD TR88-317, 19 May 1988.

404

Material Safety Data Sheet, Angus Chemical Company, with 24-hour emergency telephone number.

405/44/502

Technical Data Sheet, Angus Series TDS No. 2, 4th Edition, pp 7-8.

406/43

ANGUS responses to U.S. Army letter, dated 17 December 1986, regarding DAAA-21-86-K-0333, Technical Evaluation for TEXS Program.

407/601

Test Program Request for Tactical Explosive System (TEXS), U.S. Army ARDEC Request No. PM-MCD-3415, October 1988, prepared by AAI Corporation; and Reference D Subsystem Hardware Test, Test Plan to Support SAR on NM, Section III, September 1988.

408

"Hydraulic Hammer Calculations Regarding Tests for TEXS," Joseph Hershkowitz, January 1989.

409

"Water Hammer Test Modification Using Nitromethane for TEXS Program," SMCAR-AEE-WE(340d), 20 December 1988.

410

Test program as conducted at YUMA to evaluate Hydraulic Hammer Hazard regarding TEXS Program.

411

"Considerations Regarding Need for Nitrogen Blanket," Joseph Hershkowitz, January 1989.

412/35/611

"Sensitivity of Liquid Monopropellants to Compression Ignition: A Progress Report," N. A. Messina, L. S. Ingram, and M. Summerfield (PCRL), 19th JANNAF Combustion Meeting, Greenbelt, MD, October 4-7, 1982, Vol I, pp 521-533.

413/41

"Dynamic Loading of HAN-Based Liquid Monopropellants at Temperature Extremes," N. A. Messina, L. S. Ingram (PCRL), 24th JANNAF Combustion Meeting, pp 471-483, October 1987.

414/58

"Stability of Nitromethane," F. Bellinger, H. B. Friedman, W. H. Bauer, J. W. Eastes, W. C. Bull (Edgewood), Industrial Engineering Chemistry, 40, pp 1320-1324, 1948.

415/310/644

"Detonation in Homogeneous Explosives," A. W. Campbell, M. E. Malin, and T. E. Holland (LANL), Second ONR Symposium on Detonation, 1955.

416/321

"Shock Initiation of Nitromethane," F. E. Walker and R. J. Wasley (LLNL), UCRL-71696 Preprint, Astronautic Acta, 15, p 427, 1970.

417/331

"Shock Initiation of Nitromethane, Methyl Nitrite and Some Bis Difluoramino Alkanes," J. G. Berke, R. Shaw, and D. Tegg (SRI), Fifth Symposium (International) on Detonation, pp 237-245, 1970.

418/342

"Shock Induced Reaction in Explosives and Propellants," R. Merrifield (ERDE, GB), AD 752372, 24 pages, 1972.

419/344

"Low Order Reactions in Shocked Explosives," Neill Griffiths and V. C. Broom (RARDE), Fourth Symposium (International) on Detonation, pp 462-472, 1965.
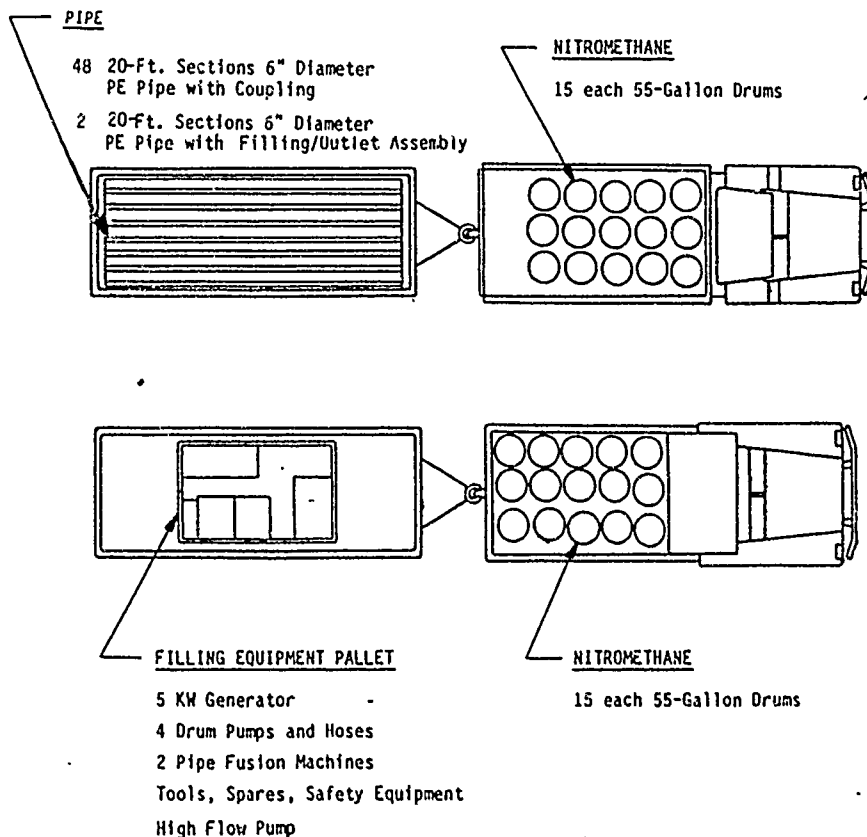
400

Reserved for future use.

401

"Proposal for TEXS, Tactical Explosive System, Nitromethane-Based Explosives Subsystem," Prepared by Angus Chemical Company, Report No. ACC-201, July 1988.

PIPE

48 20-Ft. Sections 6" Diameter
PE Pipe with Coupling

2 20-Ft. Sections 6" Diameter
PE Pipe with Filling/Outlet Assembly

NITROMETHANE

15 each 55-Gallon Drums

FILLING EQUIPMENT PALLET

5 KW Generator
4 Drum Pumps and Hoses
2 Pipe Fusion Machines
Tools, Spares, Safety Equipment
High Flow Pump

NITROMETHANE

15 each 55-Gallon Drums

Excerpts

The primary filling system utilizes the drum pumps to directly discharge the nitromethane from the drums into the pipe. Figure 3.2.1.2-1 portrays this filling system's flexibility to fill the pipe from a vehicle parked at the rear or either side of the vehicle containing the filling equipment. The secondary filling system as portrayed in Figure 3.2.1.2-2 shows the use of a high flow centrifugal pump discharging the nitromethane from the collapsible tank into the pipe. The drum pumps are used to fill the collapsible tank. This system is to be used when filling the pipe uphill.

124
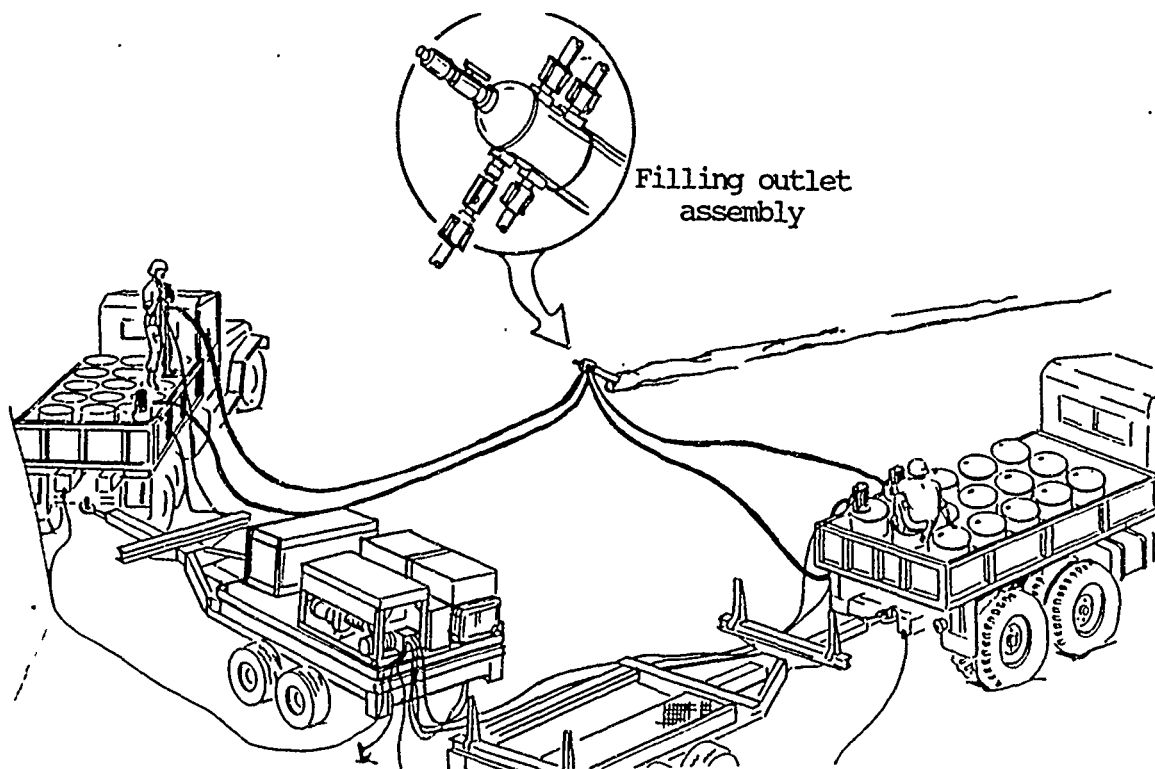
Figure 3.2.1.2-1.   Nitromethane filling operation
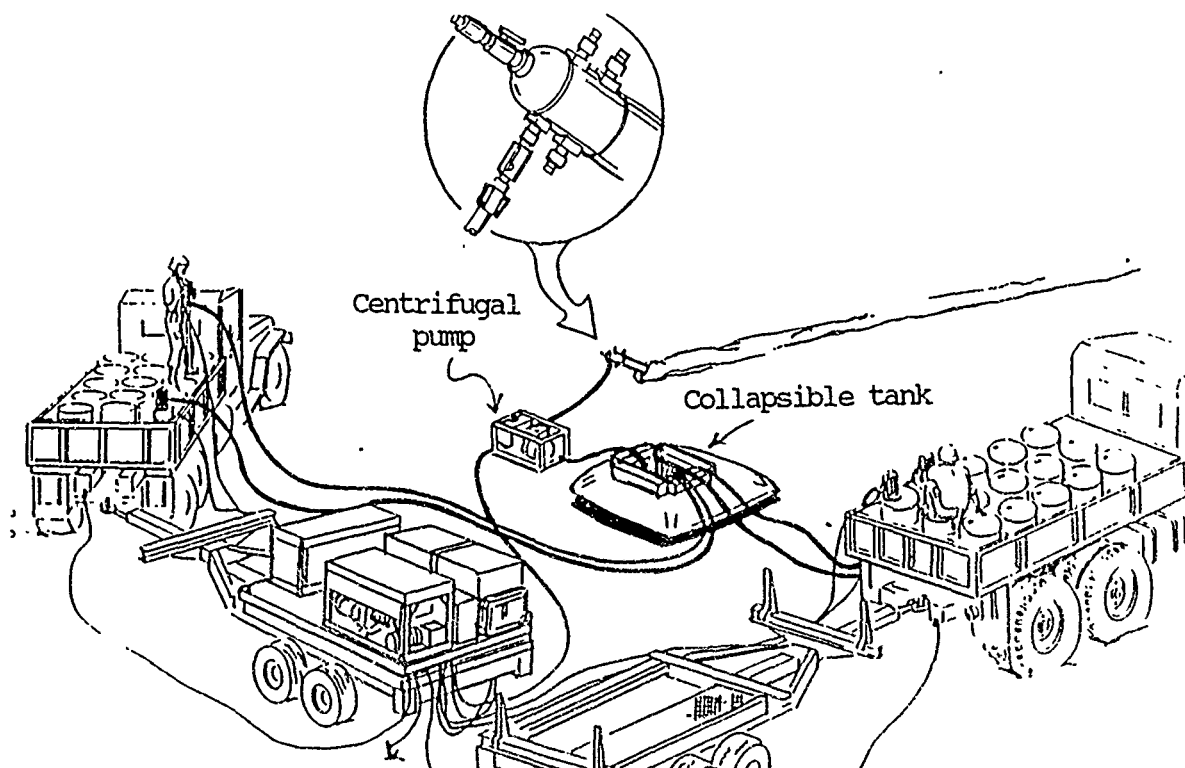
Figure 3.2.1.2-2.   Nitromethane filling operation

125

The nitromethane filling equipment for the primary system consists of four electric motor driven drum pumps and discharge hoses with quick release connectors. Each pump is rated at 50 gallons per minute at zero discharge pressure. At the estimated system back pressure of 10 psi, the pump flow rate is estimated to be 35 gallons per minute. Use of four pumps indicates a rated system flow of (4 x 35) or 140 gallons per minute. This exceeds the required flow rate of 100 gpm necessary to fill the 1500 gallon pipeline within a fifteen minute period.

The filling scenario for the primary system is as follows. The filling outlets are fitted with adapters, quick disconnectors, pressure relief valve and end caps. The filling will be done from the high end of the pipeline. The end caps at the low end of the pipeline are removed to permit air to exhaust the line during the filling operation. The pipeline pig is preinserted into the pipeline at both ends of the filling outlet assembly. All drum bungs are removed from the drums and the four pumps (two per vehicle) are inserted into the nitromethane drums. After the pumps are electrically connected to the generator and the generator is started, the discharge hoses from the pumps are connected by quick disconnects to the filling outlet. The two filling operators (one per vehicle) then start the drum pumps which forces the nitromethane into the filling outlet assembly. The low nitromethane pressure of 10 psig forces the pig to the low end of the pipeline, sweeping out the air in the pipeline. The operators index the pumps from drum to drum until the pipeline is filled.

The nitromethane filling equipment for the secondary system utilizes a high flow centrifugal pump to fill the pipe uphill. The pump is rated at 100 gallons per minute against a 75-foot pressure head which meets the flow rate of 100 gpm necessary to fill the 1500 gallon pipeline within a fifteen minute period. The filling scenario for the secondary system is as follows. The filling outlets are fitted with adaptors, quick disconnects, pressure relief valve and end caps as required. The filling is done from the low end of the pipeline. The end cap at the high end of the pipeline is removed to permit air to exhaust the line during the filling operation. The pipeline pig is preinserted into the pipeline at both ends of the filling outlet assemblies. The pig should be pushed forward of the fill port. The collapsible tank and high flow centrifugal pump are positioned, with hose attached and electrically connected. The drum pumps are used to fill the collapsible tank during the set-up phase. The high flow pump is initially primed and started to fill the pipe and pushing the pig sweeping out the air in the pipeline. The operators will continue to fill the collapsible tank while the high flow pump is filling the pipe.

The four fittings in the center section interface with the drum pump hoses by means of quick disconnects. The air vent is an automatic valve which permits air to escape to the atmosphere but closes, by means of a float, in the presence of liquid. This device permits any air behind the pig, located in the hoses and outlet assembly to be vented, thereby assuring a completely liquid-filled pipeline at the conclusion of the filling operation. Ball valves are located in the 1½ fittings which are used when filling the pipe uphill.

126

At the conclusion of the filling operation, the low end or high end of the pipeline is checked to determine the presence of the pig and the pipe plug is inserted. At the opposite end of the line, the pumps, hoses, quick disconnects, and air vent are removed and stored while the filling outlet is capped. The pipeline filling operation is now complete and awaits the emplacement of the detonator.

The function of the pig in the filling operation is to sweep all of the air out of the pipeline in order that no voids or air bubbles can occur. This will insure a full pipeline along the entire length, thus insuring consistent depth of ditching. Gravity filling without the pig might result in air pockets at rises in the line, which may terminate detonation; or at a minimum, create spots along the ditch that could be crossed.

The pipeline is purged or emptied by using water to push the emplaced pig in the pipeline as shown in Figure 3.2.1.4-1. The water is supplied by a tank truck or using an existing vehicle capable of supporting the weight of the collapsible tank filled with water. The collapsible tank or water tank truck will be filled and emptied using the high flow centrifugal pump. A pressure relief system attached at the high flow centrifugal pump will control the pipe pressure not to exceed 50 psig so adiabatic compression of the nitromethane will not occur. Two hoses and nozzles are connected to the opposite end where the nitromethane will be off-loaded from the pipeline. The nozzle has an automatic shut-off, similar to that of a gasoline pump nozzle. The operators will move from drum to drum refilling them with nitromethane. A schematic of removing nitromethane from the pipeline is depicted in Figure 3.2.1.4-2.
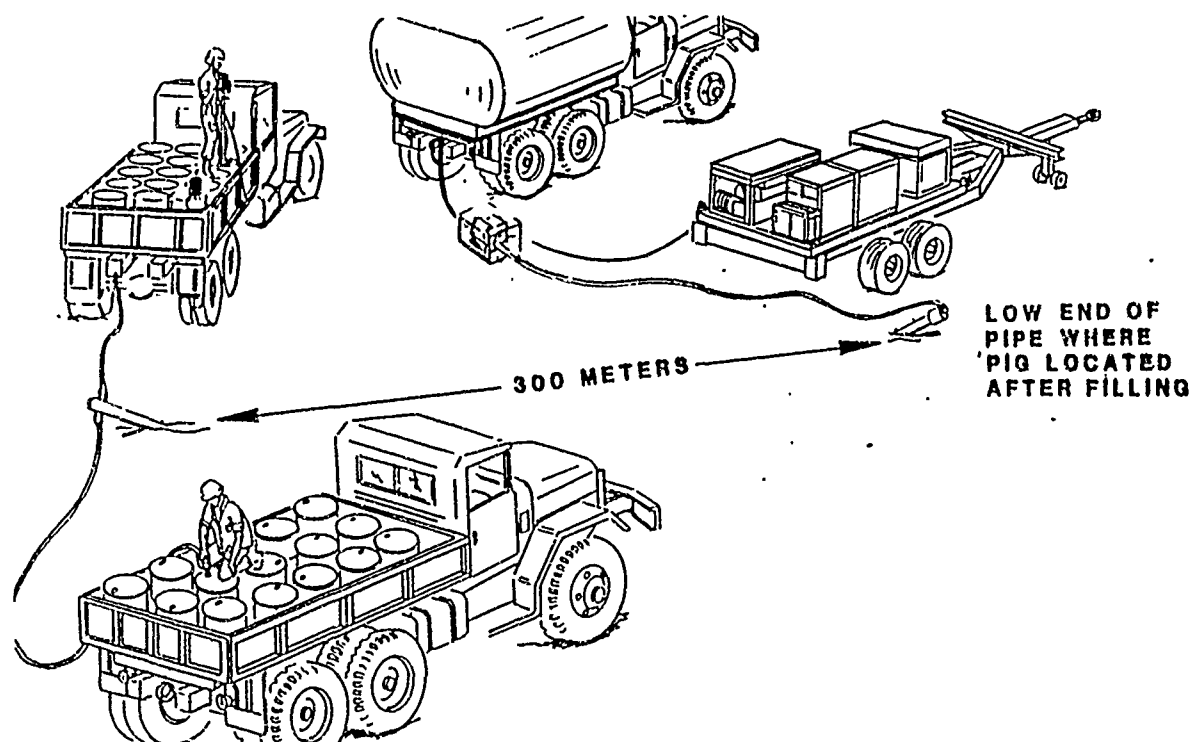

LOW END OF PIPE WHERE 'PIG LOCATED AFTER FILLING

300 METERS

Figure 3.2.1.4-1. Nitromethane removal operation

127

WATER TANK

PRESSURE RELIEF
ATTACHMENT

2 EA - REGULATING NOZZLE
OF FLOW TO DRUMS

HIGH FLOW
CENTRIFUGAL PUMP

FILL - OUTLET
ASSEMBLY

WATER   NITROMETHANE   NITROMETHANE
DRUMS

PIG WITHIN PIPE

300 METER LENGTH
OF NITROMETHANE PIPE

DISPOSABLE END
CAP WITH HANDLE

BUTT FUSED JOINT

EITHER CAP OR
BELL END READY
FOR COUPLING OPERATION

20 FOOT
PE PIPE

PIG LOCATION
IN FILL POSITION

1.5 VALVE ASSEMBLY

20 FOOT POLYETHYLENE PIPE,
WITH FILLING OUTLET ASSEMBLY

Figure 3.2.1.4-2.   Schematic of removing nitromethane from pipeline

128

The pig serves to sweep all the liquid explosive out of the pipeline at a low pressure. This insures that no explosive is left in the pipeline and all is recovered in the vehicle-mounted drums.

The pig is also used, as mentioned in paragraph 3.2.1.4, during filling of the pipeline to purge all the air from the pipeline ahead of the nitromethane. This type of pig is referred to as a "batching" or "displacement" pig. In the natural gas industry where pipelines are routinely hydrostatically tested, batching displacement pigs are used to displace the air ahead of the hydrostatic test fluid and, in turn, are used to displace the fluid after the test. The subject application is similar as it is desirable to: (1) remove the air from the pipeline during filling operation, and (2) have the capability to remove the nitromethane from the pipeline after it has been filled.

There are a variety of pigs available to meet different requirements. Cleaning pigs remove scale or debris from the inside of pipelines. Gauging pigs are used to survey the pipe. Pigs are constructed of different materials and in different configurations depending upon their use. Batching/displacement pigs are usually made of various elastomers which make them flexible but yet provide a good seal on the inside of the pipeline. The particular batching pig to be used in TEXS will be sufficiently flexible to traverse the bends in the pipe at the low and high ends. It will also pass through and maintain adequate sealing in pipe even if the pipe may have become slightly out of round due to rough handling during pipe emplacement.

The operator is prevented from overfilling the drums by a back pressure sensing device fitted in the nozzle. This nozzle is similar to those used in automobile filling stations. When the nozzle end is submerged, the pressure sensor releases the trigger mechanism to stop the liquid flow.

Nitromethane drums are capable of surviving a minimum of 10 years in controlled storage and a minimum of 2 years in open storage, with a significant safety margin. ANGUS provides the following data in support of this capability:

The production specification for nitromethane, since the start of commercial production in 1940, has always been minimum 95% by weight nitromethane and minimum 99% by weight nitromethane and minimum 99% by weight total nitroparaffins (nitromethane, nitroethane, and nitropropane). The gas chromatograph procedure currently used to determine these values has a precision of ±0.2%.

A retained sample of commercial nitromethane produced in 1940 was re-analyzed in 1986. The re-analyzed material had a nitromethane content of 96.4% and total nitorparaffin content of 99.9%, still meeting current composition criteria after 46 years, and showing no evidence of deterioration.

A sample of commercial nitromethane produced in 1954 was re-analyzed by gas chromatograph in 1971. That analysis showed nitromethane content of 95.6%, and 99.4% total nitroparaffin content. Re-analysis of the same mate-

rial in 1986 showed nitromethane content of 95.8% and 99.8% total nitroparaffin content.

The commercial nitromethane produced in 1973, which has been used as the reference standard for card-gap explosive testing since that time, was likewise re-analyzed in 1986. The analysis showed 96.9% nitromethane content and 99.6% total nitroparaffin content.

Thus, it can be stated unequivocably that production-grade nitromethane remains undeteriorated many years beyond the 10-year storage life required for the liquid-explosive component of the TEXS system.
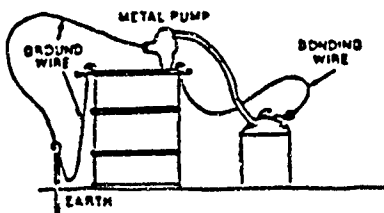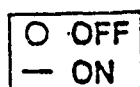
WARNING

When using a drum pump to fill cans, drums or other portable or fixed containers with flammable or combustible liquids such as gasoline, both the container being pumped from and the container being pumped to must be effectively BONDED and GROUNDED to prevent discharge of sparks of static electricity which could cause explosion.

BONDING is the electrical interconnection between containers (such as drum and a receiving can). Bonding must be completed before pumping begins. (See diagram.)

GROUNDING is the electrical connection between a container and a "constant ground." A "constant ground" would be a metal pipe or rod in contact with the earth. An underground tank and piping connected to it would be inherently grounded by nature of the installation.

Both BONDING and GROUNDING of containers of flammable liquids are required under U.S. Government OSHA regulations and National Fire Protection Association Code 77, static electricity.

Metal Pumps must be bonded to metal container or grounded, if used with plastic container.

Normal safety procedures must be used at all times when operating any piece of machinery. Do no modify or make any changes to the product without receiving written permission from Lutz Pumps, Inc.

130

402

Reserved for future use.

403/506

"Preliminary Hazard Analysis (PHA) Nitromethane and Ammonium Nitrate Based Tactical Explosive Systems (TEXS)," Billy R. Sharp, SRS Technologies, Draft Technical Report SRS/STD TR88-317, 19 May 1988.

The average decomposition temperature for Nitromethane is 411°C (771.8°F) with an average deviation of + or - 8°C.   In an early study of Nitromethane as a potential rocket propellant, it was concluded that, "The thermal decomposition of Nitromethane apparently falls into two categories, the first being normal decomposition which may be assumed to involve a simple breaking down of the Nitromethane molecule, followed by oxidation, leading to normal oxidization, or combustion products.[35] The rates of this mechanism of decomposition are measurable, and the temperature limits have been defined. The second is a high order mechanism by which nitromethane decomposes with detonation violence under certain conditions. It is this second mechanism which has not been totally defined that has given rise to unpredictable and sometimes unexplained explosions.

As already indicated, the critical temperature of Nitromethane is 315°C (599°F). Test results reviewed as a part of this PHA all indicate that detonation of Nitromethane does not occur until it has been heated above the critical temperature. However, it has been noted that decomposition irregularities always occurred at approximately 300°C (572°F). It has also been noted that at temperatures of 400°C (752°F) or higher the decomposition rate is so great that detonation by adiabatic compression has occurred, and/or decomposition becomes autoaccelerating. An interesting observation, and one which points out the unpredictability of Nitromethane, is that detonations during tests have occurred when there was no measurable decomposition before the detonation.

It has been reported that Nitromethane under long term storage at 48.9°C (120°F) or more will undergo slight thermal decomposition with the evolution of traces of Nitrogen dioxide.[36] The source of this information does not define the exact length of time referred to as "long term." In addition, no information is provided concerning the effect of this decomposition on the sensitivity or reliability of Nitromethane as an explosive, nor is there any indication as to whether the effects of this decomposition are cumulative over a storage life of 10-20 years. There is also a lack of information as to whether this decomposition will increase with age and cumulative effects over several years.

Under normal circumstances, it is unlikely that Nitromethane would be subjected to conditions which involve heat in the range of its critical temperature (599°F). However, Nitromethane exposed to a fire in a storage area or in a cargo area of a transportation vehicle (such as the hold of a ship)

could be exposed to temperatures in this range. Such a situation would represent the full range of safety hazards associated with the thermal decomposition of Nitromethane. In addition, Nitromethane in storage, even in a Temperate Zone, could be subjected to temperatures in the range of 120°F which is sufficient to cause some degree of thermal decomposition.

Burning under confined conditions is one of the most significant hazards associated with Nitromethane. Confined burning can lead to monopropellant burning and subsequent detonation, or it may lead directly to detonation.

Numerous studies have been conducted to determine the shock pressure required to initiate adiabatic compression. Generally, these studies have found that a shock in the range of 65-85 Kbars is required. This equates to a shock of approximately .94 K to 1.2 M psi. Nitromethane is shipped in Dot 17c or 17e drums because the drums will rupture and leak long before pressures of this magnitude can be achieved.

Detonation of Nitromethane by adiabatic compression can also be caused by the sudden application of high pressure air to the liquid in a heavy walled storage container,[42] and by the impact of high velocity projectiles.[43] Nitromethane sensitivity to adiabatic compression is increased significantly when air bubbles or "microspheres" (small glass, ceramic or plastic bubbles with entrapped air) are introduced to the liquid in the storage container.

If overfilled storage containers are heated and the pressure is not relieved by rupture, the sensitivity to adiabatic compression is greatly increased.

Much higher pressures can be tolerated by Nitromethane in contact with nitrogen than can be tolerated in contact with air or oxygen. For example, when the gas was oxygen, explosions have been observed with reservoir pressures as low as 250 psi. However, when the gas was nitrogen, 850 psi was the lowest pressure at which explosions occurred.

Material Safety Data Sheets provided by Nitromethane manufacturers and other sources indicate that Nitromethane can as a result of decomposition and/or contamination by other substances react to form a sodium salt which will burst into flame on contact with water.[45] Salts of Nitromethane are extremely sensitive to flame and burn readily, and they are sensitive to friction, impact, and electrical discharges.[46] In a dry state, salts of Nitromethane are extremely unstable and are highly sensitive to shock; the isolation of salts in a dry state should be strictly avoided.[47]

. . . confined liquid Nitromethane expands considerably as it is heated. Expansion of the liquid is accompanied by a corresponding increase in pressure. This pressure increase has been established at 17.5 atm (257 psi) per 1°C (approximately 1.8°F).[48] Even modest temperature increases in storage locations could cause completely filled or overfilled containers to rupture and leak. Therefore, extreme care must be taken to ensure drums of Nitromethane are not overfilled.

132

. . . if the original blanket has been lost by accident (leaking drum, loose bung closure plug, etc.) or to place a nitrogen blanket in a refilled drum.[49] Research for this PHA found no evidence to support this position. Nitrogen blankets are required for shipment and they significantly reduce the sensitivity of Nitromethane to shock and/or adiabatic compression. Therefore, it is recommended that the nitrogen blanket be restored in any drum which is opened for laboratory sample extraction, for other inspection purposes, or in cases where it is lost as a result of loose bung closure plugs.

Spills of Nitromethane, or salts which have formed in or around spills, in storage or cargo shipment areas should be neutralized and removed as soon as they are discovered. Water can be used to clean, dilute, and/or desensitize liquid spills. However, water should never be used on dry salt formations since they may ignite when they come in contact with water. Liquid spills can also be absorbed by Vermiculite or other suitable absorbent and placed in an impervious container.[50]

Compounds such as alcohols, hydrocarbons, esters, and ketones can be used to desensitize liquid Nitromethane to shock. However, research has found no recommended desensitizers for Nitromethane salts.

. . . very small quantities of water mixed with Nitromethane will make it significantly more corrosive to steel. If water is accidentally mixed with Nitromethane in steel storage drums, this could in time result in a significant problem with leaking drums. It has also been reported that small amounts of water will increase the sensitivity of Nitromethane to detonation.[52]

Nitromethane which is heated from 20°C (68°F) to its critical temperature [315°C (599°F)] will have a threefold increase in liquid volume with a corresponding increase in pressure within the storage container (drum). For example, if Nitromethane at 50°F is loaded into a perfectly rigid container (heavy confinement) and then exposed to a desert environment of 165°F, the pressure would increase to 886 atmospheres or 13,024 psi.

. . . direct sunlight, temperatures could reach the point where resulting pressures would cause virtually all drums in the location to leak. This liquid expansion - internal pressure problem is the primary reason that it is recommended that Nitromethane not be stored in direct sunlight. The latter was one of the questions which the representative from the Product Assurance Directorate (at the Task Initiation meeting) asked be addressed in this report. There is also evidence that long term storage with temperatures above 120°F (storage in direct sunlight could result in even higher temperatures) will result in some decomposition of Nitromethane.

. . . increase in temperature and pressure could significantly increase the sensitivity of Nitromethane to other forces such as mechanical shock and could cause thermal decomposition which would further increase sensitivity.

Pumping of Nitromethane can be extremely hazardous and a long list of precautions must be observed, for all operations where it is to be pumped. It is the consensus of available information sources that Nitromethane should not:

- Be pumped into a closed end pipe.

- Be pumped into a pipe where a valve may close suddenly or unexpectedly during pumping operations.

- Be pumped into a pipe where there is a small orifice or nozzle installed which could restrict or impede the flow of nitromethane.

- Be pumped into a pipe which has entrapped air pockets or air bubbles.

- Be pumped if it has been sensitized.

- Be pumped in circumstances or situations where it could be exposed to the sudden application of high pressure air.

It is also recommended by manufacturers and distributors, that positive displacement pumps not be used for pumping Nitromethane, and that pumps which can produce a pumping pressure of more than 100 psi, even under failure conditions, not be used to pump Nitromethane.[56] One information source recommends that air pressure not be used to pump or unload Nitromethane. Pumps must have seals, gaskets, and intake/output hoses which will not be destroyed or damaged by Nitromethane.

. . . , extremely conservative safety practices dictate that the discharge pressure on the pump not exceed 100 psi, in order to avoid cavitation."[59]

ANGUS Chemical Company recommends that drums of Nitromethane be stored in clusters of no more than 30 drums per cluster with a minimum of 15.2 feet between clusters and at least 75 meters (246 feet) between the storage site and the nearest occupied structure.[69] These recommendations by Angus are apparently based on tests in which 520 lb of Nitromethane was detonated approximately 17 feet from several hundred pounds of Nitromethane in another drum and there was no sympathetic detonation.

The DOD Explosives Safety Board recently reviewed the commercial (flammable liquid) and military (liquid propellant) classification for Nitromethane.[71] The Explosive Safety Board response clearly indicated that in their opinion the classification of Nitromethane as a liquid propellant is correct; that classification as a flammable liquid is not sufficient for the protection of people and property.

. . . , it appears evident at this point that plans must be made to store Nitromethane in an ammunition storage area.

134

In one test,[73] a 50 caliber bullet was fired into a drum of Nitromethane which had steel plates attached (to magnify bullet impact) and had air being vigorously bubbled through the liquid Nitromethane (to increase sensitivity to impact and/or shock). This drum detonated on impact of the bullet, however, a partially filled drum of Nitromethane located 17 feet away did not experience sympathetic detonation. The contents of the partially filled drum did burn but did not detonate. Apparently this test is the one cited by Angus Chemical Company when they say that, "Detonation of 520 pounds of Nitromethane did not lead to the sympathetic detonation of several hundred pounds of Nitromethane in a drum only 17 feet away and unprotected by barricades."[74]

In the same report, Angus also refers to two other tests conducted during this series. In one test, a 385 gram (13.5 ounce), Composition B booster (RDX and TNT with 1-4% wax) was taped to the end of a Nitromethane drum lying on its side. Detonation of the booster ripped open the drum and spilled the contents but there was no detonation of the Nitromethane. In the other test, two 380 gram (a total of 26.6 ounces) Composition B boosters were used and a detonation of the Nitromethane did occur. Angus Chemical Company also cites two other tests where 100 grams (3.5 ounces) of C-4 plastic explosive and 375 grams (13.1 ounces) of Composition B, respectively, were placed on the end of a Nitromethane drum and they failed to initiate a sympathetic detonation.

The U.S. Army, Corps of Engineers, Waterways Experiment Station has also conducted some tests of the sensitivity of Nitromethane in approved DOT drums. In these tests, four drums of Nitromethane were positioned in an upright position at ranges of 560, 670, 1360, and 1900 feet from a point where a surface detonation of 4,800 tons of Ammonium Nitrate-Fuel Oil (ANFO) explosives was initiated.[75] Surface overpressures at these locations were calculated at 150, 100, 20, and 10 psi, respectively. The Nitromethane drum at 560 feet was crushed almost flat and was moved approximately 192 feet from its original position but did not detonate. The drum at 670 feet was moved 88.5 feet and was crushed and ruptured with the loss of all of the liquid contents. The drums at the two farther locations were blown over but did not rupture. There was no detonation with any of the four drums. In another report on Nitromethane testing, Waterways Experiment Station personnel indicated that, "the two main hazards with Nitromethane are: (1) direct accidental initiation by the nearby explosion of a powerful explosive charge and (2) ignition and propellant burning of a large mass of confined liquid."[76]

It is highly unlikely that the Angus recommendation concerning a minimum distance of 75 meters between the Nitromethane storage site and occupied structures will be allowed in a military storage environment.

The threshold limit value for Nitromethane has been established at 100 ppm. Prolonged and repeated exposure to high concentrations of Nitromethane can cause respiratory tract irritation, anesthesia, liver damage, kidney disease and eye irritation. Skin contact may cause drying, cracking, or irritation. Overexposure symptoms/effects include headaches, nausea, vomiting, narcosis, anorexia, and diarrhea. Vapors of Nitromethane become very irritating at about 200 ppm, cause severe eye and respiratory irritation in

animals at 500 ppm, and have caused the death of rabbits exposed to 10,000 ppm for 6 hours. Nitromethane has also caused kidney disease in animals.

(i) Contact lens eye glasses should not be worn when working with or exposed to Nitromethane vapors.

(m) Wear a self contained breathing apparatus (SCBA) with a full facepiece operated in pressure demand or other positive pressure mode in concentrations above 100 ppm.

JH: Should this be 100 ppm? (See first sentence of this paragraph.)

This review discusses health and safety hazards that might conceivably happen when implementing TEXS. Accidental ignition, sympathetic detonation, incompatibilities, health concerns, and more, have been identified but not necessarily solved. Extensive bibliography and data sheets are included. **BD: The possible hazards should be prioritized.**

404

Material Safety Data Sheet, Angus Chemical Company, with 24-hour emergency telephone number.

ANGUS ANGUS Chemical Company 2211 Sanders Road Northbrook, IL 60062 (312) 498-6700	24-Hour Emergency Telephone (318) 665-4451
CHEMICAL NAME Nitromethane	TRADE NAME NM
CHEMICAL FAMILY Nitroparaffin	FORMULA CH_3NO_2

REACTIVITY DATA

| Shock under heavy confinement. Adiabatic compression Sensitization. Do not trap between closed valves or use positive displacement pumps to discharge nitromethane. |
| INCOMPATABILITY (MATERIALS TO AVOID)
Lead, copper or their alloys; amines, strong alkalis, strong acids. |
| HAZARDOUS DECOMPOSITION PRODUCTS
Oxides of carbon and nitrogen |
| HAZARDOUS POLYMERIZATION MAY OCCUR ☐   CONDITIONS TO AVOID
HAZARDOUS POLYMERIZATION WILL NOT OCCUR ☒ |

SPILL OR LEAK PROCEDURES

| STEPS TO BE TAKEN IN CASE MATERIAL IS RELEASED OR SPILLED
Evacuate area and remove potential sources of spark or flame. Properly protected personnel may then attempt to contain large spills and pump to salvage. Absorb unrecoverable spills with an inert solid such as sand or earth. Flush area with water. |
| DISPOSAL METHOD

Incinerate, or bury in an approved sanitary landfill. |

HEALTH HAZARD DATA

| THRESHOLD LIMIT VALUE
(PERMISSIBLE EXPOSURE LIMIT)   100 ppm (TLV and PEL) |
| EFFECTS OF OVEREXPOSURE
Liquid: Prolonged exposure can lead to mild irritation due to "defatting." Only slightly toxic by ingestion
Vapor: Headache, nausea, vomiting, narcosis. Chronic overexposure may cause liver and kidney damage. |

Material Safety Data Sheet continued on next page.

136

JH: Canister type face masks use activated carbon which absorb organic vapors that react with the carbon to produce potentially toxic quantities of nitrogen oxides.

405/44/502

Technical Data Sheet, Angus Series TDS No. 2, 4th Edition, pp 7-8.

"The pressure of confined liquid nitromethane increases 17.5 atm for every 1°C increase of its temperature. Any pockets of vapor or gas will slow the pressure rise, but small pockets can be compressed rapidly enough to heat the gas and even to ignite the nitromethane." Adiabatic compression can occur in a pipe in which the flow of liquid is impeded so that most of the kinetic energy of the moving liquid is expended in compressing a pocket of gas. "Higher pressures without explosions can be tolerated by NM in contact with nitrogen—because it cannot induce ignition and support combustion." Experiments with oxygen showed explosions with reservoir pressures as low as 250 psi, with nitrogen required 850 psi minimum. In thick-walled containers, believe 0.50 caliber high velocity bullet transfers energy to compress gas in head space causing observed explosion, but needs vapor space for explosion. For thin-wall container, explosion does not occur. Pressures necessary for monopropellant burning exceed rupture value for 55 gallon DOT 17E steel

drums. "Handling systems should be designed so that pressures cannot exceed 100 psig, even with improper operation. If higher pressures are necessary, extra precautions must be taken to prevent occurrence of adiabatic compression."

Exposure of rats to NM vapor - 13,000 ppm (33 g/m^3), in air, 6 hr - death

- 2,500 ppm, (6.3 g/m^3 in air, 4-6 hr in 4 days, died fifth day.

- 745 ppm, 8 wk decrease in rate of body weight gain, 1 month some pulmonary abnormalities.

"Standard of 100 ppm for NM was judged to provide a satsifactory margin of safety for workers exposed to its vapors."

American Conference of Government Industrial Hygienists have set 100 ppm (~ 250 mg/m^3) as threshold limit value for an 8 hour-per-day working exposure. This time weighed average accepted by OSHA.

If prolonged exposure to NM vapors above threshold occurs, need a mask supplying fresh air or self-contained breathing apparatus. Such exposure may occur "as a result of spillage." "CANISTER GAS MASKS SHOULD NEVER BE USED FOR PROTECTION FROM NM VAPORS." **JH: Such gas masks introduce a new severe hazard. (See 404.)**

JH: Calculation of vapor concentration due to vapor pressure in a confined space as a function of temperature of liquid should be done. Leak/opening drum? Measurement of vapor concentration over full field sequence required to compare with threshold.

406/43

ANGUS Responses to U.S. Army letter dated 17 December 1986 regarding DAAA-21-86-K-0333 Technical Evaluation for TEXS Program.

Question - p 13 - At 125°F, what pressure will cause adiabatic compression of NM without a nitrogen blanket? Response - Adiabatic compression refers to vapor phase. Rate of compression, heat transport away, are important. Ignition of NM vapors will occur above 785°F. Pressure must be maintained for deflagration of liquid to follow and run-up to detonation to occur. Drum rupture asserted to precede monopropellant burning. Cites Bellinger (58). Autoignition of liquid NM does not occur with pressures up to 90,000 psi. Cites Anderson (330). States presence of nitrogen blanket or absence of no consequence.

JH: Does not account for vapor presence of NM versus temperature of liquid. If splashing, setback, etc., occur, thin films in contact with nitrogen (versus air) may be less ignitable.

Question - p 15 - Discuss the filling process with respect to the pre-vention of introducing air into the pumps/pipeline during pump out of air. Response - "A centrifugal pump cannot force liquid through a full discharge line when operating on air because the pressure developed with air is signif-icantly less than the liquid developed pressure." Did experiment (described) with transparent hose to verify this. Air due to empty hoses at start purged with float principle automatic air vent. JH: **Demonstration under field conditions of full sequence required.**

407/601

Test Program Request for Tactical Explosive System (TEXS), U.S. Army ARDEC Request No. PM-MCD-3415, October 1988, prepared by AAI Corporation; and Reference D Subsystem Hardware Test, Test Plan to Support SAR on NM, Section III, September 1988.

The request lists five objectives, as below, and Reference D gives details of procedures to satisfy these objectives. JH: **Worst case scenarios are needed.**

a. To evaluate the hazard related to adiabatic compression of NM due to the maximum water-hammer effect of NM in the pumping system with various contaminants in the system.

b. To evaluate the hazard related to adiabatic compression of NM due to a down stream blockage in the system.

c. To evaluate the hazard related to adiabatic compression of NM due to a pipe blockage on the discharge side of the drum pump.

d. To evaluate any hazards associated with NM being sprayed on hot components due to a hose rupture.

e. To evaluate any hazard related to the concentration of NM fumes emanating from the storage boxes due to heavily contaminated equipment which has not been cleaned.

For a, b, and c, the following test set-up is used:
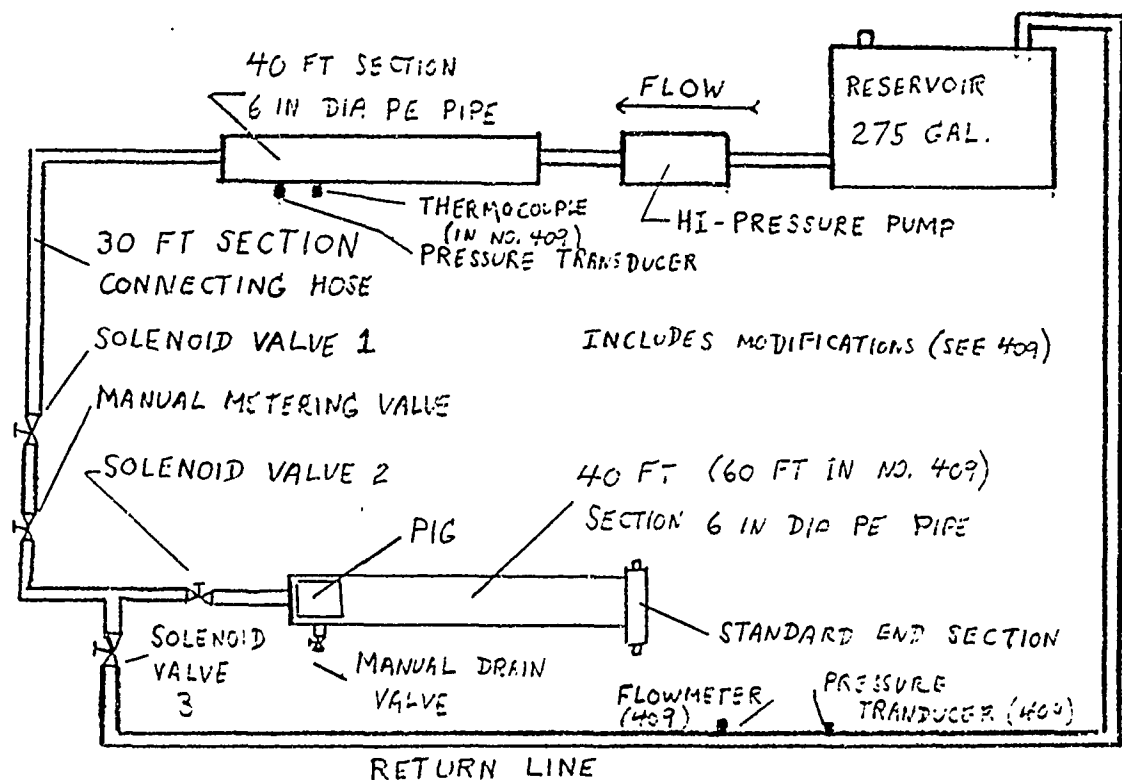
139

For d, the muffler of the generator set is to be covered by a safety shroud and NM remotely sprayed.

For e, an electric match will be used on vapor concentrations simulating the maximum level anticipated.

NOTE: Under Category 4, an analysis of water-hammer effects in the test set-up was done and recommendations made. See (408) for analysis and (409) for revised plan.

408

"Hydraulic Hammer Calculations Regarding Tests for TEXS," Joseph Hershkowitz, January 1989.

Hydraulic hammer calculations need to be combined with results of hydraulic hammer tests on nitromethane to extrapolate to the TEXS situation in order to assess the hazard for a particular case. The calculations shown here lack correct values for pipes and hoses and are based on very limited experimental data. Nevertheless the calculations indicate the manner in which the hazard may be estimated and provide guidance for a test design that provides a worst case scenario.

The equations for hydraulic hammer calculations are:

$$v_w = \left[\frac{\frac{144K}{\rho/g_c}}{1 + \frac{Kd}{Et}} \right]^{\frac{1}{2}}$$

$$P_{hh} = \frac{v \cdot v_w \cdot \frac{\rho}{g_c}}{144}$$

where:

K = fluid bulk modulus (psi)   E = pipe elastic modulus (psi)
d = internal pipe diameter (in.)   t = pipe wall thickness (in.)
v = fluid velocity (fps) P_{hh} = hydraulic hammer pressure (psi)
                                      v_w = wave velocity (fps)

ρ/g_c = fluid density $(\frac{lb \cdot sec^2}{ft^4})$

Values of above for nitromethane used here are:

K = 1.85 x 10^5 psi ρ/g_c = 2.16 $[\frac{lb\ sec^2}{ft^4}]$

A pipe of 6 inch diameter and one of 2 inch diameter are considered. It is assumed that E = 4 x 10^5 psi. This is the value for PVC which is not used for TEXS. Dimensions used are: d = 6.065   t = 0.28
                                                                                = 2.0   t = 0.14

For the 6 inch diameter pipe the results are: v_w = 1058 fps.

For   150 gpm flow v = 1.6725 fps P_{hh} = 26.5 psi
      300 gpm flow v = 3.345 fps P_{hh} = 53.1 psi

For the 2 inch diameter pipe the results are: v_w = 1273 fps.

For   150 gpm flow v = 15.1 fps P_{hh} = 288 psi
      300 gpm flow v = 30.2 fps P_{hh} = 576 psi

It follows that for a fixed pump rate (gpm), there is a much higher fluid flow velocity in the 2 inch pipe and a correspondingly higher hydraulic hammer pressure.

If the elastic modulus of the smaller diameter pipe (flexible hose) is reduced to ½ or ¼ of the value used for the larger diameter pipe, the pressure is reduced (in proportion to the reduction in v_w). For 150 gpm, 228 psi is reduced to 76 and 55 psi as the hose is made more flexible.

It follows that the effect of reduction in diameter from pipe to hose for the same pump rate can be partially offset by the flexibility of the hose.

The significance of pressures and flow rates of the TEXS application must be assessed in terms of available information on the threshold for igni-

tion (not for detonation) since ignition is not acceptable. The only relevant reference on this point is that of Hay and Watson, No. 16, which requires extensive extrapolation as described.

Hay and Watson used a steel cylinder 10.2 cm inside diameter, 15.2 cm length and 1.27 cm wall thickness with a steel plate at one end and a thin polyethylene diaphragm at the other. They introduced air bubbles with a needle. The initiating stimulus was a steel projectile 9.84 cm in diameter, 13.3 cm long, weighing 8.1 kg. For nitromethane they found that the threshold for ignition was 24 m/s, 78.75 fps.

The corresponding wave velocity and hydraulic hammer pressure follow from the equations of the previous page. For $E = 10^6$, $v_w = 22.30$ pfs, $P_{hh} = 2634$ psi or for $E = 10^7$, $v_w = 3277$ fps, $P_{hh} = 3871$ psi.

There still remains an important difference from the situation in the TEXS application. The Hays and Watson experiment had only a ½ foot length which for the wave velocities above leads to 0.224 or 0.153 (x 2) milliseconds. These pulse durations are orders of magnitude shorter than the durations for a pipe or hose whose lengths are measured in hundreds or tens of feet respectively. The ignition threshold depends on duration as well as pressure amplitude. For other factors held constant the products (p^2 x duration) is used for scaling. The limitations of this approach can be found in No. 347 of the compendium. It is important for the TEXS application to be aware that:
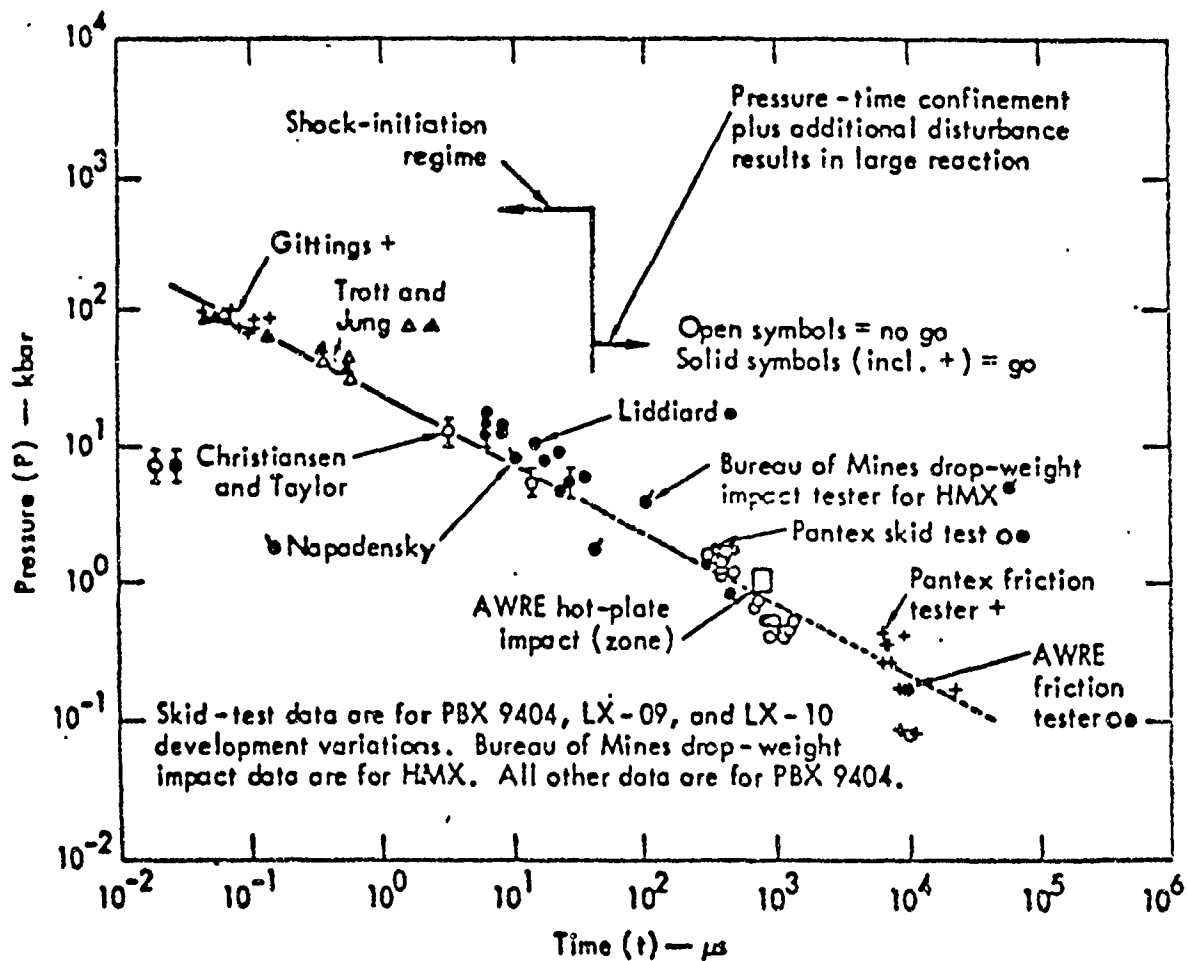
The threshold for ignition by hydraulic hammer pressure also depends on the duration of the pressure.

Extrapolation to the TEXS application cannot be done exactly with the data available; therefore, approximate values are used only to derive significance for test design modifications. From the above the threshold product for $E = 10^6$ would be $(2634)^2(0.448) = 3.1$ x 10^6 and for $E = 10^7$ would be $(3227)^2(0.306) = 3.3$ x 10^6. Use 3.2 x 10^6 as the product from Hay and Watson for ignition.

For TEXS, consider two cases: a 6 inch pipe that is 900 feet long and a 2 inch pipe that is 30 feet long. Choose the 150 gpm pump rate and initially ignore the flexibility of the hose. For pulse durations use twice the length because the pressure wave travels from the stagnation surface to the surface where release of pressure occurs and then the rarefaction wave must travel the same distance back to the stagnation surface. For the 6 inch pipe the duration would be (2 x 900)/1058 = 1700 milliseconds and for the 2 inch (2 x 30)/1273 = 47 milliseconds. Multiplying these values by the square of the corresponding pressures (P_{hh} = 26.5 or 288 psi) leads to product values of 1.2 x 10^6 and 3.9 x 10^6 (psi)(milliseconds) for the 6 and 2 inch pipes, respectively. It follows that for the same rigidity hose as pipe, 30 feet of 2 inch hose can be more hazardous than 900 feet of 6 inch pipe if the pump rate is maintained at 150 gpm. The flexibility of the hose is most important as is highlighted by comparison of the threshold numbers just derived with that derived from Hay and Watson.

142

In light of the limitations of the data used, the approximate nature of the scaling, etc., no direct conclusions should be made as to hazard. These numerics only point out that:

The test design should use the maximum length of hose that would be used in the field and it should be of the same type with respect to dimensions and flexibility.

Figure axes: Pressure (P) — kbar (vertical, 10^{-2} to 10^4); Time (t) — µs (horizontal, 10^{-2} to 10^6).

Labels on figure:
- Shock-initiation regime
- Pressure-time confinement plus additional disturbance results in large reaction
- Gittings +
- Trott and Jung ▲▲
- Open symbols = no go; Solid symbols (incl. +) = go
- Christiansen and Taylor
- Liddiard ●
- Napadensky
- Bureau of Mines drop-weight impact tester for HMX
- Pantex skid test o●
- AWRE hot-plate impact (zone)
- Pantex friction tester +
- AWRE friction tester o●
- Skid-test data are for PBX 9404, LX-09, and LX-10 development variations. Bureau of Mines drop-weight impact data are for HMX. All other data are for PBX 9404.

143

409

"Water Hammer Test Modification Using Nitromethane for TEXS Program," SMCAR-AEE-WE(340d), 20 December 1988.

The modified test set-up, shown in Figure (No. 407), will have a nitromethane (NM) pressurized pig impacting the standard end of the 60-foot section of 6 inch diameter PE pipe. The first 40 feet (closest to Solenoid Valve 2) of the 60 foot section will be straight and level. Supports 1, 3, and 4 will be equal heights. Support 2 will be higher than Support 4 to create a bow in the PE pipe. A heavy mass will rest on the center of the PE pipe to create an additional bow. The height of Support 2 and the weight of the heavy mass will be determined by the engineer prior to test. Velocity and pressure in the NM return line will be monitored. The section of 1-1/2 inch diameter hose between the 40 foot section of 6 inch diameter PE pipe and Solenoid Valve 1 will be at least as long as the longest section of 1-1/2 inch diameter hose which will be used on the TEXT System. An estimate of the length of this hose is 30 feet.

The test procedure using Solenoid Valve 1 as an obstruction will be as follows:

a. The manual metering valve is set in full open position.

b. Personnel are moved to a remote location.

c. Solenoid Valves 1 and 3 are open and Solenoid Valve 2 is closed.

d. The high pressure pump is turned on.

e. Nitromethane is allowed to circulate for 10 minutes.

f. Solenoid Valve 1 is closed.

g. After allowing the high-pressure pump to run 10 minutes, the pump is turned off.

h. The test will be performed 30 times per test sample.

The test procedure using the pig in the 60 foot 6 inch diameter PE pipe will be as follows:

a. The manual metering valve is set in the full open position.

b. Personnel are moved to a remote location.

c. Solenoid Valves 1 and 3 are open and Solenoid valve 2 is closed.

d. The high pressure pump is turned on.

e. Nitromethane is allowed to circulate for 10 minutes.

f.   Simultaneously, Solenoid Valve 3 is closed and Solenoid Valve 2 is opened.

g.   After allowing the high-pressure pump to run 10 minutes, the pump is turned off.

h.   The pipe is then drained and the pig is pushed back to its initial position using a rod. The pig is reused in the next trial.

i.   The test will be performed 30 times per test sample.

Whenever personnel are exposed to nitromethane fumes, an air sampling device is to be used to monitor the exposure concentration of nitromethane. Time of exposure is recorded. The air sampling device should give readings during entire time of exposure. If these readings are above the threshold limits set by OSHA, proper precautions should be taken.
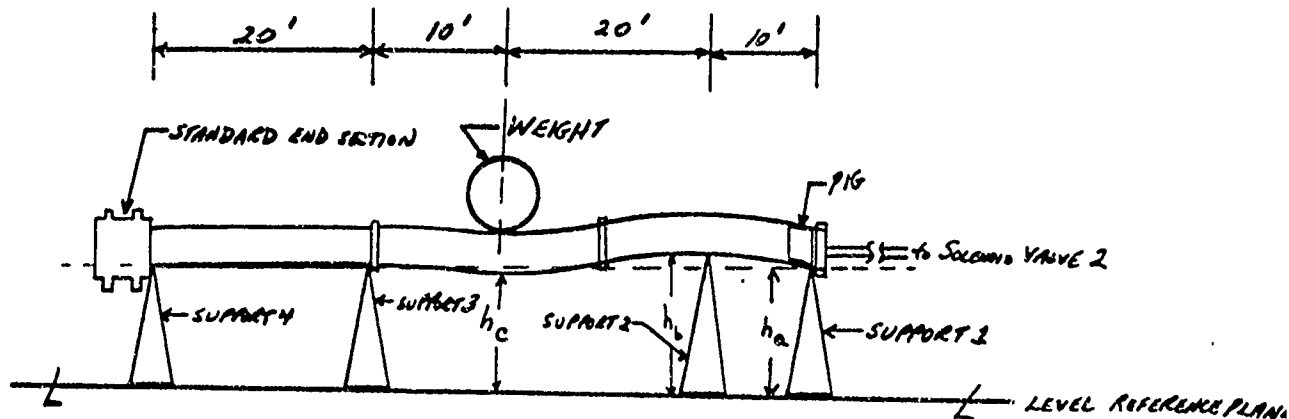
FIGURE 2

SUPPORT DIAGRAM FOR THE 60-FOOT SECTION OF 6-INCH DIAMETER PE PIPE

145

410

Test program as actually conducted at YUMA to evaluate Hydraulic Hammer Hazard regarding TEXS Program (currently underway).

411

"Considerations Regarding Need for Nitrogen Blanket," Joseph Hershkowitz, January 1989.

1 <u>Liquid motion</u> → cavitation within liquid
    froth at surface   + Kinetic energy added
    entrapped gas in pumping

2 <u>Sudden stop</u>   → compression at high rate

3 <u>Ignition</u>   bubble size, froth   Ignition is less likely if
                        vapor content   • air has been replaced by
                        gas   nitrogen.

                                          ◦ growth impeded by nitrogen

4 <u>Local growth of reaction</u>   ◦ bubble profile and contents

                                     ◦ transport into liquid and to other
                                       bubbles leading to cooperative effects

- -

5 Pressurization adequate | 6 <u>Vulnerability to enemy fire</u>
  <u>for monopropellant burning</u> |
                                    |
            ANGUS | Local action sufficiently
           position | rapid that drum cannot burst
                                    | in time so that detonation
  <u>Venting by drum rupture</u> | follows.
                                    |
                  quenches |
◦ <u>slows burning</u> ◦ reaction |
◦ NM exits drum   in drum |
  ------------------------------ |
                                    |
  <u>Venting Inadequate</u> |
                                    |
  Burn rate in small volume |
◦ so rapid that deflagration |
  continues. |
                                    |
◦ Transition   Late drum burst with
  to detonation ◦ quench and NM scattered
                    (explosion)

146

Appears prudent to improve situation at steps 3 and 4 _if feasible_. The ANGUS position in 5 does not allow for the unanticipated use, such as stacking of drums, dropping of drum into hole, etc., in the field. It also ignores the hazards in the pumping process and vulnerability situation where dissolved nitrogen in NM (_if it occurs_) alters sensitivity due to cavitation or froth.

Further--detonation is entirely unacceptable.
But--deflagration of the NM (without detonation) is still very undesirable regarding burn hazard, toxicity, spill, secondary fires.
Therefore--there is reason to take steps to reduce likelihood of 3 and 4 above.

NITROGEN BLANKET RELEVANCE

16   Projectile driven by compressed air within steel barrel (10.2 cm i.d., 3.3 cm long). Explosion criterion: cylinder unfolded or in pieces, significant blast and complete consumption of liquid. Bubbles in liquid in range 0.05 to 0.2 cm and number density 0.5 to 10 cm^{-3}. Threshold velocity for NM was 24 plus or minus 2 m/sec.

19   Gap test for cavitated liquids. Higher threshold values with argon, = 1.67, and reverse for propane, = 1.13 compared to those observed for air and nitrogen, = 1.4. Threshold gap values are enhanced with oxygen (even though gamma values are about same as for air).

21   Impact sensitivity tests on NM with trapped bubbles. Difference of results for air and nitrogen shows that the chemical nature of the gas is important.

23   NM in presence of 0.2, 0.4, 0.8 mL air bubbles to rapid compression by gas driven piston. Positive result represented essentially complete decomposition; negative unaffected sensitivity of NM was 10.4 plus or minus 1.7 kg-cm/mL. (NM one order more sensitive than hydrazine.) Kinetic energy of piston given in kg-cm. Volume of chamber was 1.3 mL. Sensitivity is in terms of mL of gas bubble volume. (See 44 and 46 regarding effect of nitrogen versus oxygen contact with NM.)

25   Rapid compression apparatus on isopropyl nitrate (NOT NM) but diluted vapor with N_2, Ar, CO_2, air or combination within bubble. In inert gas, only decomposition of vapor occurs; in air oxidation, is also important. Although not done for NM it follows directly that NM vapor (NM has high vapor pressure) will react more in presence of non-inert gas during adiabatic compression of bubble with vapor.

26   Dissolved gases change the viscosity, density, and compressibility of liquid. Infers this could be a factor in differences observed in tests with falling weight measuring sensitivity versus power into liquid observed for air and nitrogen pressurization.

37   "Jarring a liquid can first cause cavitation followed by pressure
      strong enough to ignite the bubbles by compression heating. This
      aggregate will rapidly pressurize, leading to a strong deflagration or
      detonation event, depending upon external conditions."

39   Bubble profile that exists at time of any compression wave and nature
      of pressurization/rate is critical.

43   Pressure must be maintained for deflagration of liquid to follow and
      run-up to detonation to occur. Drum rupture asserted to precede mono-
      propellant burning. States presence of nitrogen blanket or absence of
      no consequence.

44   "The pressure of confined liquid nitromethane increases 17.5 atm for
      every 1°C increase of its temperature. Any pockets of vapor or gas
      will slow the pressure rise, but small pockets can be compressed
      rapidly enough to heat the gas and even to ignite the nitromethane."
      Adiabatic compression can occur in a pipe in which the flow of liquid
      is impeded so that most of kinetic energy of the moving liquid is
      expended in compressing a pocket of gas. "Higher pressures without
      explosions can be tolerated by NM in contact with nitrogen—because it
      cannot induce ignition and support combustion." Experiments with oxy-
      gen showed explosions with reservoir pressures as low as 250 psi, with
      nitrogen required 850 psi minimum. Also affects bullet sensitivity.

50   A froth formed at the liquid hydrazine-gaseous nitrogen interface as
      the liquid traveled through the gas ullage. "It is believed that com-
      pression of the froth at the dead head produces adiabatic heating and
      thermal runaway."

52   A surge pressure of 3600 psi resulted for water accelerated with a push
      pressure of 200 psi into a line pressurized with nitrogen at 0.1 psia.
      Tests done with 8 inch column of liquid accelerated by a 500 psi push
      pressure into a 15 inch long glass chamber pressurized with nitrogen at
      12.4 psi. Video showed froth "created by Taylor instabilities at the
      liquid-gas interface resulting in Helmholtz mixing of gas and liquid."
      Froth maximizes surface and, under compression, heat transfer is very
      rapid leading to rapid thermal runaway. Container rupture occurred for
      hydrazine, not for water.

57   Equipment provided control of compression rate, piston travel, velocity
      and bounce. Piston velocities 5.7, 13.4, and 17.3 fps. There was
      more liquid agitation at 17.3 fps. Ignitions at high piston velocities
      were more violent as a result of the extensive liquid-gas interface
      obtained.

58   Dropped 200 gm hammer in 10 tests. It was found that NM would explode more easily when an atmosphere of oxygen instead of air filled the space. Also, a harder hammer blow was required to cause explosion of NM when this space was filled with nitrogen instead of air or oxygen. The sudden application of 2000 psi high pressure gas on NM is likely to cause an explosion even though the NM is free to flow. The use of 1230 psi air pressure under the same conditions appears to be safe. If NM is forced into a closed pipe by 850 psi, it will explode even if nitrogen is used on both sides of the liquid column. Samples of NM that resulted from 50°C storage tests were more sensitive to explosion by impact than original material.

62   Vapor supply mechanism's important focal point rests in hot gas-surface energy interchange, e.g., bubble compression, film boiling, and energy transfer to condensed phase. Vaporization rates depend on the surface temperature and the external gas pressure. Nitrogen mixed with vapor retards chemical runaway.

412/35/611

"Sensitivity of Liquid Monopropellants to Compression Ignition: A Progress Report," N. A. Messina, L. S. Ingram, and M. Summerfield (PCRL), 19th JANNAF Combustion Meeting, Greenbelt, MD, October 4-7, 1982, Vol I, pp 521-533.

Bubbles may be brought into the chamber during loading or may be formed by cavitation during the filling process. Visualization was done for a piston ram system. The liquid is somewhat compressible, and the compression wave propagates through the column with a finite velocity, stagnating the fluid to meet boundary condition. The pressure pulse collapses cavities producing hot spots. "Water hammer" peaks of 1000 psi and pressurization rates of 10 Kpsi/msec are obtained. However, for those liquids considered, ignition has not occurred. Propellant was not re-used because of bubble content and possible change in rheological properties. Used a compression ignition sensitivity tester to do tests versus bubbles in liquid. Found a finite induction time needed for pressure generation due to gas evolution, and runaway reaction always occurred well afterward. Confinement time under pressure is thus a factor. JH: **Not for NM. Parallel studies for TEXS are needed.**

"Dynamic Loading of HAN-Based Liquid Monopropellants at Temperature Extremes," N. A. Messina, L. S. Ingram (PCRL), 24th JANNAF Combustion Meeting, pp 471-483, October 1987.

A transparent chamber is used to evaluate rapid fill (through gun valve) of liquid propellant from ambient down to -55°C, in which range viscosity increases by three orders of magnitude. From 20° to -40°C some ullage is observed. Between -40°C and -55°C change occurs--"discrete bubbles distributed though the liquid at -55°C assume non-spherical shapes; injection times increase by a factor of 3 to 5; large pockets of undivided ullage occur." **JH: This is not NM, but it suggests critical viscosity occurs at a temperature, and pumping and bubble characteristics change sharply. Effects for centrifugal pump will be different. Although not done, equipment can do swirl injection.**

"Stability of Nitromethane," F. Bellinger, H. B. Friedman, W. H. Bayer, J. W. Eastes, W. C. Bull (Edgewood), Industrial Engineering Chemistry, 40, pp 1320-1324, 1948.

Application of interest transferred 20 gallons of liquid to a chamber in 0.75 second or less. Studies three NM's: (1) 96% NM, remainder mostly nitropropane, small amounts of nitroethane, acetic acid, and water; (2) 96% NM balance as (1); (3) NM purified by fractionation. Dropped 200 gram hammer in ten tests, and assigned 0.1 for detonation, 0.05 for partial detonation, zero if none. **JH: Explosion rather than detonation believed to have occurred.**

Drop Height (cm)	20	30	40	50
NM (1)	0.00	0.10	0.50	0.65
(2)	0.05	0.40	0.60	
(3)	0.20	0.45	0.90	
Nitroglycerin	0.70			

Shorter hammer fall means NM detonates more easily. Note that pure NM (3) is more sensitive.

It was found that NM would detonate more easily when at atmosphere of oxygen instead of air-filled space. Also, a harder hammer blow was required to cause detonation of NM when the space was filled with nitrogen instead of air or oxygen. **JH: Here again is basis for nitrogen ullage reinforced by possibility of froth mechanism. See (50)-(53) and (57).** The sudden application of 2000 psi high pressure gas on NM is likely to cause a detonation even though the NM is free to flow. The use of 1230 psi air pressure under the same conditions appears to be safe. If NM is forced into a closed pipe by 850 psi pressure, it will detonate even if nitrogen is used on both sides of the liquid column. Did tests with 0.50 caliber machine gun at 100 yards, except 200 yards for full 55 gallon drains. NM in 0.25-inch steel wall containers will not be detonated unless 2% catalyst is present. Incendiary

ammunition causes explosions and fires even in thin-walled containers. **JH: If incendiary ammunition is part of the threat, this is most serious.** An empty NM drum (one still containing NM vapor) will explode when hit by incendiary ammunition. NM is relatively inert to tracer fire. Table VII gives full results.

Samples (1) and (2) stored at 50°C in closed container created a partial pressure due to absorption from the air above NM; judged as due to impurities. The samples of NM that resulted from the 50°C storage tests were more sensitive to detonation by impact than the original material. Addition of small quantities of gasoline is proposed as a practical means to decrease the sensitivity of NM to detonation. **JH: It is important to test properties at temperature extremes and also after storage periods at temperature extremes.** Note that work was done at Guggenheim Aeronautics Laboratory of California Institute of Technology (GALCIT). See (59),(60), and references cited.

415/310/644

"Detonation in Homogeneous Explosives," A. W. Campbell, M. E. Malin, and T. E. Holland (LANL), Second ONR Symposium on Detonation, 1955.

Used NM in 55 gallon drums from Commercial Solvents specified as NM by weight minimum 95, Nitroparaffins 99, Specific Gravity 25/25°C 1.1283, Acidity as acetic acid 0.01, Water 0.052. "To further guard against the presence of alkaline materials which might act out as sensitizers, the NM was redistilled at reduced pressure from sulfuric acid and stored in glass bottles." The temperature (°C) dependence of density given by $d_T = 1.1645 - 1.337 \times 10^{-3} T - 1.15 \times 10^{-6} T^2 + 3.8 \times 10^{-9} T^3$. Raising temperature increases detonation velocity but decreasing density decreases detonation velocity for liquid explosives. The combination results in NM in a decrease of -3.7 m/sec/°C with increase of T. Provides data on diameter effect in NM versus T in glass tubes and for the failure diameter. For latter, over the range $-12°F$ to $98°F$ the failure diameter varied from 15 mm to 35 mm, increasing as the initial temperature was lowered. **JH: Thus for HVD below 1-½ inch at $-12°F$, failure to propagate would occur. For TEXS at low T limit, a constriction to 2 inch diameter must be avoided.** "Plastic tubes were not used because of the possibility of contamination of the explosive by solvent action." **JH: Is this a problem with polyethylene tubes used for TEXS?** "Failure occurred by non-luminous areas spreading inward from the confining walls and choking off the detonation process." Provides test configurations for liquids for detonation velocity, diameter, and confinement versus temperature.

416/321

"Shock Initiation of Nitromethane," F. E. Walker, R. J. Wasley (LLNL), UCRL-71696 preprint, Astonautic Acta, 15, 427, 1970.

Proposes that in both homogeneous and heterogeneous initiation, Arrhenius kinetics are not applicable at 60 Kbar and that there enters a

"shock-induced non-equilibrium temperature in a shock front that causes a higher-than-equilbrium reaction rate in and near the shock front." Figure 1 shows the interrelation of pressure and duration for NM shock initiation comparing curve with experimental points, and includes points at 6 and 10 Kbar.

JH: This data ultimately led to the $(\frac{p^2 t}{\rho_o U})$ shock initiation criterion rather than the explanation offered here. The data points for 6 and 10 Kbar are NOT otherwise available, as this was given to authors as a private communication. The points in Figure 1 could be used to derive the criterion value and extend it to lower pressures. However, later and more complete data is available (322).

Shock initiation at Kbar levels is significant for TEXS with respect to vulernability to enemy attack, particularly in drums.

417/331

"Shock Initiation of Nitromethane, Methyl Nitrite and Some Bis Difluoramino Alkanes," J. G. Beake, R. Shaw, and D. Tegg (SRI), Fifth Symposium (International) on Detonation, pp 237-245, 1970.

NM is CH_3NO_2; methyl nitrite is CH_3ONO. The CH_3O - NO bond strength is more than 20 Kcal/mole weaker than the CH_3 - NO_2 bond. For constant shock pressure, the reaction time for liquid methyl nitrite is significantly less than the reaction time for NM. In all cases, the reaction times decreased as the initiating shock pressure increased in the range 70 to 130 Kbar. At 86 Kbar the reaction time was found to be 0.7 μsec whereas LANL found 2.26 μsec. Reducing the impurities in NM from around 3% to less than 0.5% had no effect on the reaction time. All of the results can be explained in terms of homogeneous thermal explosion theory. For NM, preshock temperatures of 16 to 40°C were used. Other data extends range to 5°C. Figure 6 gives reaction times versus peak pressures for 5°C and 40°C. At the higher temperatures, the reaction times were lower at the same shock pressure. Failure to propagate occurs at 76 Kbar at 40°C and at 81 Kbar at 5°C. Shock sensitivity to initiation reduces with decrease in temperature. JH: TEXS application regarding initiation of NM at cold T by extrapolation.

418/342

"Shock Induced Reaction in Explosives and Propellants," R. Merrifield (ERDE, GB), AD 752372, 24 pages, 1972.

The modified gap test was used to determine the threshold for burning which for long duration lower pressures was found to be much lower than for initiation of detonation. The Hugonist "adiabat" for NM is given as U = 1.56 + 1.96 u where U is shock velocity and u is particle velocity, both in mm/μsec. Figure 15 compares results for different sources. The threshold pressure for detonation is given as 104 Kbar for NM which is higher than the usual ~85 Kbar value. This is attributed to the possible difference in

152

purity of the samples. "The particular NM sample used here was part of an old consignment originally intended for use as a fuel. It is probably typical of the quality of NM samples which might be handled or stored in bulk. **JH: This raises the question of whether old NM might be more difficult to initiate. This effect would be accentuated at the low temperature extreme.** A threshold pressure for burning was not found for NM. The axial velocity of the material blow-off after 50 mm of travel (U_a) were obtained. Figure 5 shows U_a versus P_g (pressure incident) for NM as a smooth curve until 109 Kbar where detonation leads to a sharp discontinuity. Therefore, there is no particular threshold for a self-propagating detonation, but increasing reaction responds to increasing incident pressure. **JH: With energy intensifiers, there may be a threshold for burning followed by run-up to LVD.**

419/344

"Low Order Reactions in Shocked Explosives," Neill Griffiths and V. C. Broom (RARDE), Fourth Symposium (International on Detonation, pp 462-472, 1967.

When a homogeneous or heterogeneous explosive is shocked, the energy can be released either rapidly or slowly depending on the explosive properties and intensifiers and on the intensity of the shock. If sufficient energy is contributed to the shock front it will accelerate, or if energy in the rear is sufficient it will overtake the shock--in both cases and for combinations, detonation can be achieved. If insufficient energy is contributed, the shock will decay. The cavitation depends on the duration of the shock wave. "If the pulse length is gradually increased, a balance can eventually be obtained between energy lost and energy produced and a pseudostable detonation is set up." The critical pulse length is related to the reaction zone length in the propagation of detonation. An intense but sufficiently short shock pulse may not lead to initiation. **JH: The initiating system for TEXS, in order to be positive and reproducible, must have a pulse length at least a multiple of the induction time and over a volume a multiple of failure dimensions.**

CATEGORY 5

HEALTH HAZARDS

REFERENCES

500

Summary of Category 5 - Health Hazards, for Compendium of Nitromethane Data relevant to the Tactical Explosive System (TEXS) Program, Brigitta Dobratz, February 1989.

501

Nitromethane Safety Assessment Report, Angus Chemical Company, June 1988.

502

Technical Data Sheet, TDS No. 2, 4th edition, Angus Chemical Company, no date.

503

"Handling of Nitroparaffins," C. E. Watts and W. C. Goinner (Commercial Solvents Company), Chem Engr News, 30, p 2344, 1952.

504

"Health and Environmental Effects Profile for Nitromethane," Environmental Protection Agency, Cincinnati, OH, Report PB88-180518/XAB, 1988.

505

"2-Nitropropane Casues Cancer in Rats," NIOSH, Chem Engr News, 10, May 2, 1977.

506/403

"Preliminary Hazard Analysis (PHA) Nitromethane and Ammonium Nitrate Based Tactical Explosive Systems (TEXS)," Billy R. Sharp, SRS Technologies, Draft Technical Report SRS/STD TR88-317, 19 May 1988.

507-509

Reserved for future use.

510

"Biochemical Toxicology of Environmental Agents, A. deBruin (Netherlands), Elsevier, NY, pp 106-107, 1976.

511

"Clinical Toxicology of Commercial Products - Acute Poisoning," R. E. Gosseline, et al., Dartmouth Medical School.

512/747

"Compendium of Safety Data Sheets for Research and Industrial Chemicals, Part III," L. H. Keith and D. B. Walters, Nitromethane VCH Publishers, Deerfield Beach, FL, pp 1240-1241, 1985.

513

"Dangerous Properties of Industrial Materials," N. J. Sax, Van Nostrand Reinhold Company, NY, pp 2029-2030, 1984.

514

"Encyclopedia of Occupational Health and Safety," L. Parmeggiani, editor, International Labour Office, Geneva, Switzerland, 3rd Ed., 1983.

515

"Hazardous and Toxic Effects of Industrial Chemicals," M. Sittig, Noyes Data Corporation, Park Ridge, NJ, 1979.

516/749

"Hazardous Chemicals Data Book," G. Weiss, editor, Noyes Data Corporation, Park Ridge, NJ, 1980.

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"The Merck Index," M. Windholz, editor, Merck and Company, Rahway, NJ, 1983.

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"Registry of Toxic Effects of Chemical Substances," 1985-1986 Edition, D. V. Sweet, 1985-1986 Edition, U.S. Department of Health and Human Services, Public Health Service, Cincinnati, OH, 1987.

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"Evaluation of Solid Sorbents for Sampling Aliphatic and Aromatic Nitro Compounds in Work-Room Air," K. Andersson, J. O. Levine, and C. A. Nilsson (Sweden), Chemosphere, 12, pp 377-384, 1983.

521/745

"Recommended Methods for the Purification of Solvents and Tests for Impurities: Nitromethane," J. F. Coetzee and T. H Chang, Pure Appl Chem, 8, pp 1542-1545, 1986.

522

"Subchronic Inhalation Toxicity of Nitromethane and 2-Nitropropane," T. R. Lewis, C. E. Ulrich, and W. M. Busey, J Environ Pathol Toxicol, 2 (5), pp 233-249, 1979.

523/775

"Nitromethane," A. Makovky and L. Lenji, Chem Revs, 58, pp 627-644, 1958.

524

"Munitions-Related Substances of Potential Concern as Airborne Pollutants," W. R. Mura, et al., U.S. Army Medical Bioengineering Research and Development Laboratory, Fort Detrick, Frederick, MD, Report TR 7409, AD-B001198L, December 1974.

525

"Oral Mononitromethane Poisoning," A. Prerovska and V. Styblova (Czechoslovakia), Pracovni Lekar, 16, pp 168-170, 1964.

526

"Hygienic Assessment of Nitromethane and Other Nitroparaffins in Connection with Sanitary Protection of Water Reservoirs," V. G. Subbotin (Russia), Gig Sanit, 32 (9), pp 9-13, 1967. (In Russian)

500

Summary of Category 5 - Health Hazards, for Compendium of Nitromethane Data relevant to the Tactical Explosive System (TEXS) Program, Brigitta Dobratz, February 1989.

Items starting with 501 are corporate entries. Excerpts from handbooks begin with 510 and articles by individual authors begin with 520. Alphabetical order by source, title, author is followed within each set respectively.

The health hazards evaluated from the above are:

• Toxicity

OSHA and Federal threshold limit value for inhalation of vapor in air is 100 ppm/8-h day, that is ~250 mg/m^3 (Refs. 501-502, 512-513, 515-516, 518, 520-524). Only Ref. 520 specifies this value for workroom air. Mura measured NM vapor concentration in air, which escaped through the buildings' scrubber vents, at 0.012 ppm (0.026 mg/m^3), 0.12 km outside the boundary of HAAP (Ref. 524). Above 7.3% volume in air, an explosive mixture is formed (Ref. 521).

The toxic hazards rating is moderate for inhalation (Ref. 511, 513) and high for ingestion (Ref. 513). Gosseline (Ref. 511 estimates the lethal dose for a 70-kg human to be between 1 oz and 1 pt (1 lb). Effects of ingestion are detailed in Ref. 525, the central nervous system being severely affected.

• Environmental Impact

EPA (Ref. 504) has found existing data insufficient to determine an acceptable daily intake or carcinogenic potency factor. However, EPA requires notification in case of a release of ≥ 1000 lb, based on chronic toxicity, as required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA).

In Russia, Subbotin determined a maximum permissible concentration in potable water of 0.005 mg/L for odor detection (Ref. 526). Odor threshold is <200 ppm, but water pollution toxicity is not known (Ref. 516).

• Personnel Protection

No toxic effects on eyes or skin were observed up to 200 mg/m^3 doses (Ref. 501). Because NM is soluble in water, washing body, clothes, and surroundings with soap and water will remove spills (Refs. 500, 512, 516). Prolonged or frequent repeated exposure to NM may lead to drying and irritation of the skin, and to respiratory problems, nausea or vomiting, etc., from inhalation (Refs. 501, 511, 512, 516). Some NM vapor is exhaled

cleavage of the molecule. This results in formation of formaldehyde and nitrite, the latter being oxidized to nitrate and eliminated in the urine (Ref. 510).

Because of the hazards associated with inhalation of NM vapor and possible ingestion, protective clothing and breathing apparatus are musts when working with NM, especially in tanks and buildings and near spills and fires (Refs. 501, 502, 514, 515, 516, 520, 522, 523). Gloves made of PVA may provide protection (Ref. 512).

Suggestions for Additional Research

A major impurity in NM is 2-nitropropane (2-NP); its OSHA threshold limit value for inhalation of vapor in air is 25 ppm (90 mg/m^3) (Refs. 505, 513, 515, 516). Different batches from different suppliers contain varying amounts of impurities. (This will be discussed in Category 7.) The OSHA/ Federal limit value for NM vapor inhalation of 100 ppm/8 h in air has been found adequate, but no data seem to exist on the influence of 2-NP with its 25-ppm limit. For NM materials specification, it might be desirable to determine the maximum amount of 2-NP allowable in the product. 2-NP has been identified as a potential carcinogen (Refs. 505, 512, 513, 515).

• The following personnel and environmental safety hazards should be researched and evaluated:

1. Explosion hazards (Ref. 516),

2. Effects/pollution of soil, air, and water (Refs. 516-526),

3. Deleterious effects of impurities and contaminants in NM.

Information on these topics, relevant to the safe use of NM in TEXS, seems to be sketchy or nonexistent.

After all categories of the compendium have been completed, it may be possible to evaluate data relevant to 1 through 3 above that pertain to health hazards. For example, fire and explosion/detonation are covered in Categories 1 and 3, effects of temperature and pressure changes on the properties of NM are compiled in Category 7.

501

Nitromethane Safety Assessment Report, Angus Chemical Company, June 1988.

The OSHA standard of 100 ppm NM vapor inhaled per 8 h was judged an adequate limit for worker safety. No toxic effects were observed on eyes or skin up to 200 mg/m^3 doses. Prolonged or frequent repeated exposure of the skin may lead to drying and mild irritation, but no allergic reactions or other adverse effects were noted. For general hygiene, wash with soap and water and change clothes after a spill. Oral ingestion tests with animals showed mild pathological changes in the animals' livers with a 0.25% dose in

showed mild pathological changes in the animals' livers with a 0.25% dose in water but not with a 0.1% dose. Human hazard is very slight; no cases have been reported. **BD: See Prerovska and Styblova (525) for oral NM poisining.**

502

Technical Data Sheet, TDS No. 2, 4th edition, Angus Chemical Company, no date.

NM is similar to other commercial solvents in its effects on humans regarding vapor inhalation. The OSHA standard of 100 ppm (~250 mg/m^3) of air inhaled in an 8-h period is deemed adequate. If working inside a tank, around spillage, or a fire, a mask or self-contained breathing apparatus should be used, but it must be equipped with a non-organic vapor filter, i.e, do not use activated carbon/charcoal filters. **BD: See (520, 523) for evaluation of activated charcoal (also 503).**

503

"Handling of Nitroparaffins," C. E. Watts and W. C. Goinner (Commercial Solvents Company), Chem Engr News, 30, p 2344, 1952.

Toxicity: 100 ppm vapor in air. Precautions given for prolonged industrial exposure. Storage Stability: Completely stable under anhydrous conditions. Corrosion is inhibited by small amounts of phosphoric acid or monobutyl phosphate. Certain lead pigments cause pressure buildup in stored cans, but with basic lead carbonate and lead sulfate are okay. Impact Stability: NM in air or N$_2$ will explode when heated for 16.5 min at 605°F in tightly closed containers. Bullet impact causes detonation in heavy walled (0.25-in. steel) containers. Dry Salt Hazard: Nitroparaffins are slightly acidic in water due to nitronic acid. The acid forms salt with inorganic bases. The dry salts are explosive. Use of masks supplying fresh air is recommended. Hopcalite and activated carbon-type respirators must not be used.

504

"Health and Environmental Effects Profile for Nitromethane," Environmental Protection Agency, Cincinnati, OH, Report PB88-180518/XAB, 1988.

Existing data are insufficient to determine an acceptable daily intake or carcinogenic potency factor. The quantity of NM for which notification is required in case of a release is 100 lb, based on chronic toxicity. This is a requirement of the Comprehensive Environemntal Response, Compensation and Liability Act (CERCLA). **BD: Only abstract is available (GRAI8813).**

505

"2-Nitropropane Casues Cancer in Rats," NIOSH, <u>Chem Engr News</u>, <u>10</u>, May 2, 1977.

2-NP produces liver cancer in rats after six months exposure at ~200 ppm. The current OSHA limit is 25 ppm. Therefore, it would be prudent to handle 2-NP as if it were a human carcinogen.

506/403

"Preliminary Hazard Analysis (PHA) Nitromethane and Ammonium Nitrate Based Tactical Explosive Systems (TEXS)," Billy R. Sharp, SRS Technologies, Draft Technical Report SRS/STD TR88-317, 19 May 1988.

Refer to 403/506 of Category 4.

507 - 509

Reserved for future use.

510

"Biochemical Toxicology of Environmental Agents, A. deBruin (Netherlands), Elsevier, NY, pp 106-107, 1976.

Mononitroalkanes are very readily absorbed from the lungs. After absorption, a variable fraction is eliminated unaltered via exhaled air. The fraction retained is rapidly metabolized through oxidative cleavage of the molecule, with generation of nitrite ion and aldehyde formation. Intermediate nitrite is largely oxidized yielding nitrate, which appears in the urine. Denitration of NM might proceed similar to that evidenced in molds:

$$CH_3NO_2 + H_2O + O_2 \rightarrow CH_2O + H^+ + NO_2^- + H_2O_2$$
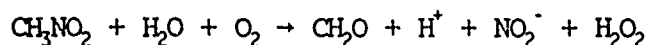
BD: **Denitration reaction occurs with water. No handling caution given.**

511

"Clinical Toxicology of Commercial Products - Acute Poisoning," R. E. Gosseline, et al., Dartmouth Medical School.

NM has toxicity rating 3: moderately toxic. Probable lethal oral dose is 0.5 - 5 g/kg or, for a 70-kg human, between 1 oz and 1 pt (1 lb). NM is also mildly irritating to skin and mucous membranes. Men exposed to NM vapors may suffer from anorexia, nausea, vomiting, diarrhea, and/or headaches. BD: **See also Sax (513).**

"Compendium of Safety Data Sheets for Research and Industrial Chemicals, Part III," L. H. Keith and D. B. Walters, Nitromethane VCH Publishers, Deerfield Beach, FL, pp 1240-1241, 1985.

NM is a toxic skin irritant. Symptoms may be dermatitis, pulmonary irritation, weakness, ataxia, convulsions, liver and kidney injury, nausea, vomiting, diarrhea. Federal standard is 100 ppm. Antidotes are listed for skin and eye contact, inhalation, and ingestion. Store in an explosion-proof, dark area. Dispose of waste in sealed plastic bags. PVA gloves may give skin protection when handling NM.

Changes in NM - Soluble in H_2O, ethanol, ether, acetone; usual physical properties are listed. NM can react with amines, strong acids and oxidizers, and with alkalies.

BD: This information on data sheets would be useful to have available for emergencies in the lab, plant, and field. See also (516).

2-NP physical properties are listed. DOT classification is flammable liquid. Vapors are toxic and irritating to eyes, skin, and mucous membranes. Exposure causes headache, dizziness, nausea, and diarrhea. Threshold limit value (TLV) is 25 ppm. Rinse with water if exposed and breathe fresh air.

513

"Dangerous Properties of Industrial Materials," N. J. Sax, Van Nostrand Reinhold Company, NY, pp 2029-2030, 1984.

Threshold Limit Value (TLV): 100 ppm in air.

Toxic Hazards Rating (THR): High - oral
                            Moderate - inhalation

In humans it may cause anorexia, nausea, vomiting, and diarrhea, also kidney injury and liver damage.

Fire Hazard: Dangerous when exposed to heat, oxidizers, or flame.

Disaster Hazard: Emits toxic fumes of NO_x when heated to decomposition. Very explosive.

Explosion Hazard: Moderate when shocked or exposed to heat or flame.

For 2-NP, the corresponding values are: TLV - 25 ppm
                                        THR - mutagenic

May cause gastrointestinal disturbances to liver and kidneys.

Fire Hazard: Moderate when exposed to heat, open flame, or oxidizers.

Explosion Hazard: May explode on heating. May react violently with chlorosulfonic acid and oleum.

For NE, the corresponding data are: TLV - 100 ppm
                                      THR - moderate - oral

Causes liver and kidney injury.

Fire Hazard: Same as NM and propionitrile, for which TLV is 14 mg/m^3 for nitriles.

514

"Encyclopedia of Occupational Health and Safety." L. Parmeggiani, editor, International Labour Office, Geneva, Switzerland, 3rd Ed., 1983.

NM, an aliphatic nitro compound, is relatively stable under ordinary conditions but it should be handled in well-ventilated areas, and workers should wear protective equipment. NM is soluble in H$_2$O and very soluble in ethyl alcohol and ether.

515

"Hazardous and Toxic Effects of Industrial Chemicals," M. Sittig, Hoyes Data Corporation, Park Ridge, NJ, 1979.

Permissible Federal Exposure Limit is 100 ppm (250 mg/m^3) for NM, 25 ppm (90 mg/m^3) for 2-nitropropane (a major impurity of NM). Effects of vapor inhalation range from skin, eye, and respiratory-tract irritations to damage to the central nervous sytem, liver, and kidneys. 2-NP should be treated as if it were a carcinogen. One U.S. cigarette contained 0.53 μg NM.

516/749

"Hazardous Chemicals Data Book," G. Weiss, editor, Hoyes Data Corporation, Park Ridge, NJ, 1980.

Chemical and physical properties are listed. Listed as flammable liquid with TLV of 100 ppm. Vapor is irritating to eyes, nose, and throat, and liquid is harmful if swallowed. Fire hazard: Flashback may occur along vapor trail or explode if ignited in confined space. 2-NP has TLV of 25 ppm. Chemical and physical properties are listed, as is fire hazard.

BD: The information on data sheets would be useful to have available for emergencies in the lab, plant, and field. See also (512).

517

"The Merck Index," M. Windholz, editor, Merck and Company, Rahway, NJ, 1983.

Preparation and properties are briefly stated. NM forms an explosive sodium salt.

For guinea pigs and mice, lethal concentrations are LD_{50} in air and 100 ppm and 1.44 g/kg orally.

518

"Registry of Toxic Effects of Chemical Substances," 1985-1986 Edition, D. V. Sweet, 1985-1986 Edition, U.S. Department of Health and Human Services, Public Health Service, Cincinnati, OH, 1987.

No toxic effects were noted on NM inhalation in monkeys. Intravenous effects in dogs were in liver and respiratory system. Oral effects in dogs were in liver and urinary system. OSHA standard is limit of 100 ppm in air. DOT regulation: flammable liquid.

519

Reserved for future use.

520

"Evaluation of Solid Sorbents for Sampling Aliphatic and Aromatic Nitro Compounds in Work-Room Air," K. Andersson, J. O. Levine, and C. A. Nilsson (Sweden), Chemosphere, 12, pp 377-384, 1983.

Threshold limit values in workroom air, issued by the American Conference of Governmental Industrial Hygienists, Cincinnati, OH, 1982, are for NM 250 mg/m^3/8 h average. Analytical methods are sorbents and chromatography. Activated charcoal gives very poor recovery (NM 55%). Amberlite XAD-7 is excellent (NM 85%).

BD: These data apply to indoor usage. Many respirators are equipped with charcoal filters, which are not suitable or safe to use with NM.

521/745

"Recommended Methods for the Purification of Solvents and Tests for Impurities: Nitromethane," J. F. Coetzee and T. H. Chang, Pure Appl Chem, 8, pp 1542-1545, 1986.

NM is a dipolar aprotic solvent with high relative permittivity and weak electron-donor ability. If nitronate ions are allowed to form salts in

NM, especially with heavy metals, explosion will result. Impurities are identified and purification procedure given. Toxicity and Explosion Hazard: NM acts as moderate irritant when inhaled (threshold limit in air 100 ppm); forms explosion mixture above 7.3v/v% in air. Distillation is hazardous, especially when traces of bases and heavy metal ions are present. Dried NM may explode when adding fresh molecular seives. In purification of commercial NM, water is easily removed. Relatively high concentrations of homologs lower its density and increase its viscosity.

BD: Impurities can cause explosion, increase viscosity. Formation of nitronate salts in NM increases sensitivity. Fumes/vapors are moderately irritating when inhaled.

522

"Subchronic Inhalation Toxicity of Nitromethane and 2-Nitropropane," T. R. Lewis, C. E. Ulrich, and W. M. Busey, J Environ Pathol Toxicol, 2 (5), pp 233-249, 1979.

NM vapor is an eye and respiratory tract irritant and is mildly narcotic. Experiments on rats and rabbits verify the adequacy of the OSHA standard of 100 ppm NM. Conclusions are based on experiments with rats.

NP in the same type of experiment, was given an OSHA standard of 25 ppm because it was found to be more toxic than NM.

523/775

"Nitromethane," A. Makovsky and L. Lenji, Chem Reos, 58, pp 627-644, 1958.

Toxicity - NM is not significantly absorbed by the skin. When using respirators, do not use the activated-carbon type because of NM's high heat of adsorption. Hopcalite, used in respirators to convert CO to CO_2, affects NM to an extent that may cause fire. Thermal decomposition (Category 7) - Of gas additions tested, O_2 accelerates decomposition, H_2 slows it. Low-pressure and high-pressure decomposition mechanisms are described. Basic oxides catalyze the reaction, acidic ones do not. Photolysis reactions are also given. Additions of small amounts (trace to 2%) of a heavy metal (Cr, U, W) increased the explosion temperature from 312°C to 323.9°C, or 366.5°C. Corrosion rates are low; attacked are SS and Al alloys > 0.0001 in./yr and mild steel at ~0.0005 in./yr. Most other common metals and alloys are attacked at rates too low to cause structural failure. Resistant to attack are bakelite, chlorinated rubber, polyethylene, and 464CS. Water increases corrosiveness. Physical contants are tabulated. **JH: Note significance of corrosion data for TEXS application.**

524

"Munitions-Related Substances of Potential Concern as Airborne Pollutants," W. R. Mura, et al., U.S. Army Medical Bioengineering Research and Development Laboratory, Fort Detrick, Frederick, MD, Report TR 7409, AD-B001198L, December 1974.

A threshold limitation of 100 ppm (250 mg/m^3) was mentioned based on Machle's study. Concentrations of NM vapors were estimated at 0.012 ppm (0.026 mg/m^3) at 0.12 km outside the boundary of HAAP. This value is much below the threshold values. Reference is also made to concentrations of 0.8 to 5 ppm NM found in automotive emissions.

BD: **Atmospheric, airborne pollution appears to be no problem from the low concentrations that escape through the buildings' scrubber vents.**

525

"Oral Mononitromethane Poisoning," A. Prerovska and V. Styblova (Czechoslovakia), Pracovni Lekar, 16, pp 168-170, 1964.

A suicidal attempt is described, manifested by epileptiform paroxysms. The neurological picture involves a central symptomatology with abnormal electroencephalographic tracings.

BD: **Only abstract available (CA61:12536h).**

526

"Hygienic Assessment of Nitromethane and Other Nitroparaffins in Connection with Sanitary Protection of Water Reservoirs," V. G. Subbotin (Russia), Gig Sanit, 32 (9), pp 9-13, 1967. (In Russian)

The threshold for affecting the sanitary regime of a stream is 5 mg/L. Maximum permissible concentration should be 0.005 mg/L based on the possibility of forming chloropicrin from MeNO$_2$ during water chlorination.

LD$_{50}$ in mice (mg/kg)	95^ ± 122
LD$_{50}$ in rats (mg/kg)	900 ± 80
Coefficient of cumulation	1.88
Threshold for odor detection (mg/L)	9.06

BD: **Only abstract available (CA67:120062). I surmise that the maximum permissible concentrations are intended for human environmental water protection.**

CATEGORY 6

TESTS

REFERENCES

601/407

Test Program Request for Tactical Explosive System (TEXS), U.S. Army ARDEC Request No. PM-MCD-3415, October 1988, prepared by AAI Corporation; and Reference D Subsystem Hardware Test, Test Plan to Support SAR on NM, Section III, September 1988.

602

Reserved for results of tests at YUMA.

603/27

"Detonation Sensitivity of Bubbly Liquid Propellants for Guns," L. C. Elmore, R. N. Boyd, L. J. Gee, and G. C. Quinn (PSI), 16th JANNAF Combustion Meeting, Vol 1, pp 285-326, September 1979.

604

"Ignition and Combustion Study of NOS-365 Liquid Propellant," (PSI), Pulsepower Systems Inc., Final Report TR 156, February 1979.

605/22

"The Ignition of Certain Monopropellants by the Adiabatic Compression of Bubbles. Part 1: A Theoretical Analysis of Adiabatic Compression Effects Produced by Sudden Pressurization of a Liquid Column Containing a Vapour Space," P. D. Verschoyle, (ERDE, GB) Report No. 13/R/58, March 1959, (AD 215075) [U68192].

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"Compression Sensitivity of Monopropellants," G. A. Mead, ARS Journ. pp 192-198, March 1959.

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"Shock Sensitivity of Liquid Propellants: The Exothermic Decomposition of Isopropyl Nitrate Under Rapid Compression," P. Beeley, P. Gray, and J. F. Griffiths, Seventeenth Symposium (International) on Combustion at University of Leeds, England, August 20-25, 1978.

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"Adiabatic Compression Measurements of Bubble Entrained in Gel Propellant," Neale A. Messina and Larry S. Ingram (PCRL), Princeton Combustion Research Laboratories, Inc., Final Report PCRL-FR-87-007, 30 October 1987.

609/29

"Compression Ignition Sensitivity of Liquid Monopropellants at Temperature Extremes," N. A. Messina, L. S. Ingram, and S. A. Traicarico (PCRL), 25th JANNAF Combustion Meeting, October 1988.

610/31

"Compression-Ignition Sensitivity Studies of Liquid Monopropellant in a Dynamic-Loading Environment," N. A. Messina, L. S. Ingram, P. E. Camp, and M. Summerfield (PCRL), 16th JANNAF Combustion Meeting, Monterey, CA, September 10-14, 1979, pp 247-284.

611/35/412

"Sensitivity of Liquid Monopropellants to Compression Ignition: A Progress Report," N. A. Messina, L. S. Ingram, and M. Summerfield (PCRL), 19th JANNAF Combustion Meeting, Greenbelt, MD, October 4-7, 1982, Vol I, pp 521-533.

612/36

"The Role of Physical Properties in Dynamic Loading Processes and Bubble Collapse of Liquid Monopropellants for LPG Applications" N. A. Messina, H. H. Tseng, L. S. Ingram, and M. Summerfield (PCRL), 21st JANNAF Combustion Meeting, Laurel, MD, October 1-4, 1984, Vol II, pp 515-527.

613/38

"Sensitivity of Liquid Monopropellants to Compression Ignition," N. A. Messina, L. S. Ingram, M. Summerfield (PCRL), 18th JANNAF Combustion Meeting, Vol II, pp 269-287, 1981.

614/42

"Nitromethane Based Monopropellants," U.S. Air Force Technical Report AFRPL-TR-81-17, 88D176-D183, May 1981.

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Nitromethane TEXS System, Safety Assessment Report (SAR), June 1988, ANGUS Chemical Company.

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"Explosive Decomposition of Hydrazine by Rapid Compression of Gas Ullages," D. Baker, et al., 1988 JANNAF Safety and Environmental Protection Subcommittee Meeting, Chemical Propulsion Information Agency, May 1988.

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"Compression Ignition Studies of a Liquid Monopropellant," A. H. Mitchell and H. A. Kirshner, AIAA Journal, 1, 9, pp 2083-2087, September 1968.

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"Classification of Liquid Gun Propellants and Raw Materials for Transportation and Storage," William J. Cruice, Hazards Research Corporation, Contract Report ARBRL-CR-00454, May 1981.

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"Function and Safety Tests of NOS-365 Monopropellant," H. Dean Mallory (NWC), Naval Weapons Center, NWC TP-5940, April 1977.

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"Development of a Simple Stability Test for Monopropellants Utilizing a Detonating Cup and Heavy Confinement," Richard S. Egly and Quentin R. Jeffries, Western States Section Combustion Institute, Paper WSCD 65, 35, 1965.

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"Physical, Stability, and Sensitivity Properties of Liquid Explosives," K. Scribner, R. Elson, R. Fyfe, J. P. Cramer (LLNL), Sixth Symposium (International) on Detonation, August 24-27, 1976, ACR-221, ONR, Dept. of the Navy, pp 466-474.

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"Impact Sensitivity Test for Liquid Explosives," Bureau of Explosives Design, ICC requirements for Class A Desensitized Liquid Explosives in accordance with para 73.53 of ICC Tariff No. 10.

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The Shock Sensitivity of Explosive Films," R. Watson, J. Ribovich, F. C. Gibson (BuMines), Pyrodynamics, 6, pp 391-51, 1968.

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"A Compilation of Hazards Test Data for Propellants and Related Materials," Radford Army Ammunition Plant, Hercules Incorporated, Final Engineering Report (on PE-489), RAD 100.10, selected pages.

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"Large Scale Drop and Projectile Impact Sensitivity Tests of Nitromethane," R. T. Keyes (R. S. Egly involved), Intermountain Research and Engineering Co., Inc., Report No. 11-NM2, July 16, 1958. PA U134842

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"Drop-Weight Impact Sensitivity of Explosives," Carl Boyars and Donald Levine (NSWC), Pyrodynamics, 6, pp 53-77, 1968.

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"Bureau of Mines Internal Ignition and Gap Tests," R. J. Mainiero and J. E. Hay, Pittsburgh Research Center Internal Report No. 4521, April 1985.

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"Chemical Sensitization of Nitro Compounds," M. D. Cook and P. J. Haskins (RARDE, GB), Combustion and Detonation Phenomena, 19th International Annual Conference, June 29 - July 1, 1988, Karlsruhe, Germany, pp 85-1 to 85-8.

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"Initiation and Growth of Detonation in Liquid Explosives," F. C. Gibson, C. R. Summers, C. M. Mason, and R. W. Van Dolah (BuMines), Third Symposium on Detonation, pp 436-454, 1960.

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"Detonations in Liquid Explosives - The Low Velocity Regime," R. W. Watson, C. R. Summers, F. C. Gibson, and R. W. Van Dolah (BuMines), Fourth Symposium (International) on Detonation, pp 117-125, 1965.

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"The Effect of Physical and Chemical Properties on the Sensitivity of Liquid Explosives," J. E. Hay, J. Ribovich, F. H. Scott, and F. C. Gibson, Fourth Symposium (International) on Detonation, pp 412-425, 1965.

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"Effect of Cavitation on the Shock Sensitivity of Liquid Explosives," V. Krishna Mohan and J. Edmund Hay, BuMines Seventh Symposium (International) on Detonation, pp 373-384, 1981.

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"Investigation of Detonations in Liquid Hydrazines," H. Beeson and M. Plaster, 1988 JANNAF Safety and Environmental Protection Subcommittee Meeting, Chemical Propulsion Information Agency, May 1988.

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"Detonation in Homogeneous Explosives," A. W. Campbell, M. E. Malin, and T. E. Holland (LANL), Second ONR Symposium on Detonation, 1955.

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"Reaction Zone Measurements in High Explosive Detonation Waves by Means of Shock-Induced Polarization," R. R. Ljsselstein (Netherlands), Combustion and Flame, 66, pp 27-35, 1986.

647 - 650

Reserved for future use.

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"Detonation Waves in a Liquid-Gas Bubble System," A. I. Sychev, Combustion, Explosion and Shock Waves, pp 365-372, November 1985.

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"Measurements of the Shock Adiabatics of Cast TNT, Crystalline RDX and Nitromethane," V. S. Ilyukhin, P. F. Pokhil, O. K. Rozanov, and N. S. Shvedova Proceedings of the Academy of Sciences of the USSR, Physics, Vol 131, No. 4, pp 793-796, April 1960.

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"Parameters of Supercompressed Detonation for Nitromethane and a Solution of Nitromethane with Bromoform," M. F. Gogulya and N. G. Demchenko, Combustion, Explosion and Shock Waves, 22, pp 106-111, July 1986.

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"Study of the Process of Initiation of Detonation of Explosives by Shock Waves Using the Method of Electrical Conductivity," A. N. Dremin and A. N. Mikhailov (USSR), Combustion, Explosion and Shock Waves, 9, pp 367-370, March 1975.

601/407

Test Program Request for Tactical Explosive System (TEXS), U.S. Army ARDEC Request No. PM-MCD-3415, October 1988, prepared by AAI Corporation; and Reference D Subsystem Hardware Test, Test Plan to Support SAR on NM, Section III, September 1988.

The request lists five objectives, as below, and Reference D gives details of procedures to satisfy these objectives. **JH: Worst case scenarios are needed.**

a. To evaluate the hazard related to adiabatic compression of NM due to the maximum water-hammer effect of NM in the pumping system with various contaminants in the system.

b. To evaluate the hazard related to adiabatic compression of NM due to a down stream blockage in the system.

c. To evaluate the hazard related to adiabatic compression of NM due to a pipe blockage on the discharge side of the drum pump.

d. To evaluate any hazards associated with NM being sprayed on hot components due to a hose rupture.

e. To evaluate any hazard related to the concentration of NM fumes emanating from the storage boxes due to heavily contaminated equipment which has not been cleaned.

For a, b, and c, the test set-up used is shown in Category 4 in figure with 407.

For d, the muffler of the generator set is to be covered by a safety shroud and NM remotely sprayed.

For e, an electric match will be used on vapor concentrations simulating the maximum level anticipated.

NOTE: Under Category 4, an analysis of water-hammer effects in the test set-up was done and recommendations made. See (408) for analysis and (409) for revised plan.

"Detonation Sensitivity of Bubbly Liquid Propellant for Guns," L. C. Elmore, R. N. Boyd, L. J. Gee, and G. C. Quinn (PSI), 16th JANNAF Combustion Meeting, Vol I, pp 285-326, September 1979.

Loaded a transparent chamber. Caviation occurred in the inlet passage resulting in a fine bubble structure. Water hammer pressure (approximately 1300 psi) completely changed the bubble structure in the chamber causing bubbles to disappear or become extremely small. When chamber pressure was dropped to ambient, the expanded bubbles were estimated to be no larger than 0.003 inch diameter.

Did modified card gap tests to determine the sensitivity of bubbly propellants to strong shock stimuli. The applied shock was supported by reaction in the liquid, but a detonation did not occur—a sustained velocity of 2430 m/sec was achieved.

Ignition by spark, pyrotechnic, and explosive, at ambient and 60°C, for liquid without and with bubbles 1 - 3 mm and 4 - 7 mm sizes.

JH: This is a comprehensive study, but not on NM.

604

"Ignition and Combustion Study of NOS-365 Liquid Propellant," (PSI), Pulsepower Systems Inc., Final Report TR 156, February 1979.

The objective of these tests was to measure reaction rate and pressure in the liquid propellant contained in heavy wall tubes and ignited by a pyrotechnic device. The value to the TEXS program is in the techniques used. The propellant was heated to 60°C by heat lamps. Air bubbles were introduced through two 0.007-inch diameter orifices supplied via a two-stage regulator. The air bubbles were allowed to migrate through the propellant column and escape through a hole at the top. Manifold air pressure was adjusted until the volume displaced by the bubbles was 1/8 inch. The test facility used a hole lined with corrugated pipe in the earth into which the charge was lowered and covered with a dome (details in Figures 2 and 3). The pyrotechnic ignition feature is shown in Figure 4.
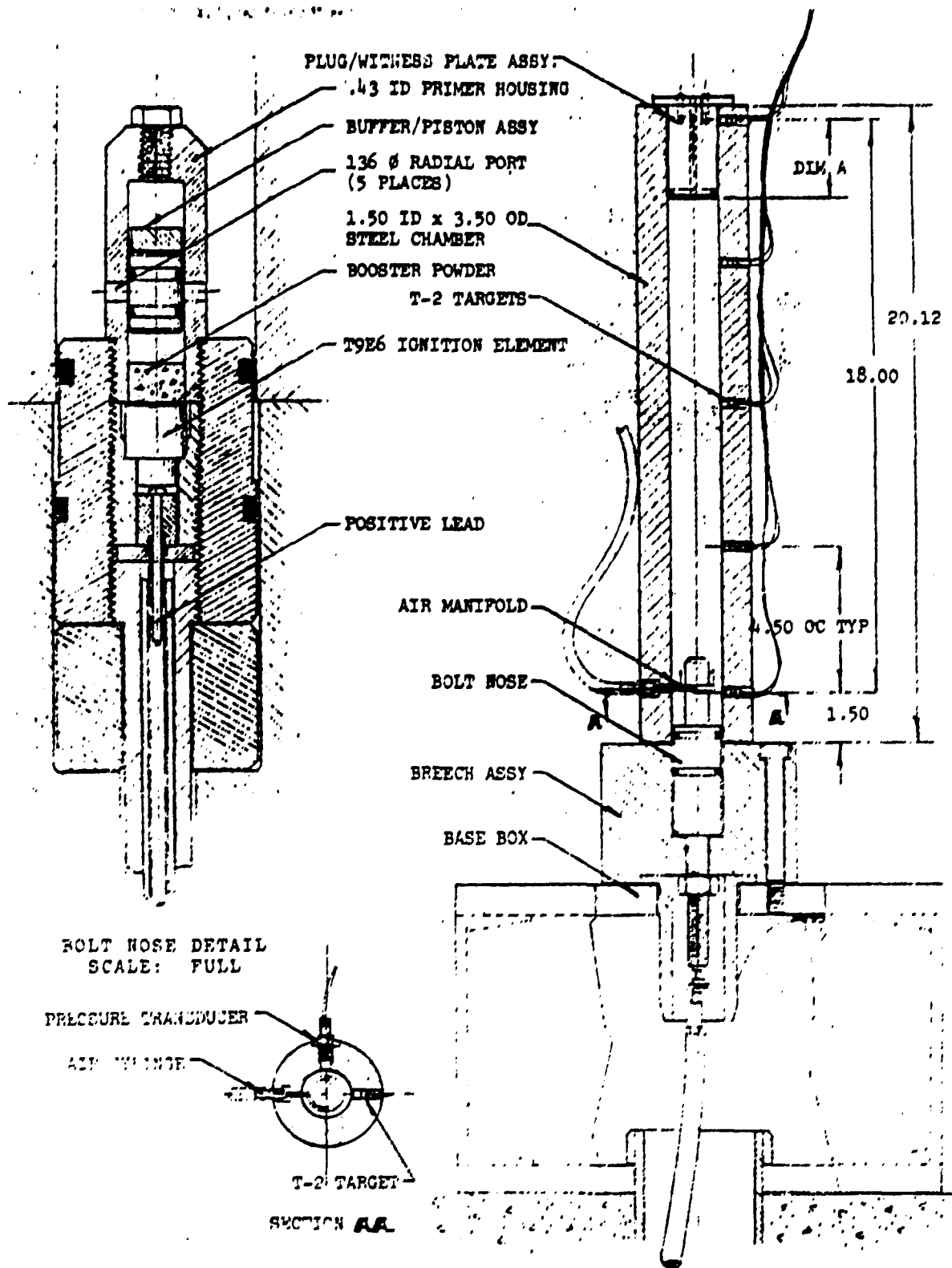
PLUG/WITNESS PLATE ASSY.
.43 ID PRIMER HOUSING
BUFFER/PISTON ASSY
136 Ø RADIAL PORT
(5 PLACES)
1.50 ID x 3.50 OD
STEEL CHAMBER
BOOSTER POWDER
T-2 TARGETS
T9E6 IGNITION ELEMENT

POSITIVE LEAD

AIR MANIFOLD
BOLT NOSE
BREECH ASSY
BASE BOX

DIM A

20.12

18.00

4.50 OC TYP

1.50

BOLT NOSE DETAIL
SCALE: FULL

PRESSURE TRANSDUCER
AIR SYRINGE

T-2 TARGET

SECTION AA

Figure 4. Pyrotechnic ignition test fixture

179

"The Ignition of Certain Monopropellants by the Adiabatic Compression of Bubbles. Part 1: A Theoretical Analysis of Adiabatic Compression Effects Produced by Sudden Pressurization of a Liquid Column Containing a Vapour Space," P. D. Verschoyle, (ERDE, GB) Report No. 13/R/58, March 1959, (AD 215075)[U68192].

Picatinny Arsenal U68192 Pt. 1. Pt. 2 is classified, but contains unclassified material included here as the paragraph below.

(U) The relation between the driving pressure and rate of pressure rise in a bubble will normally be so complex that in a practical application it will not be possible to calculate the conditions in a bubble. In order to determine whether ignition is likely, it will be necessary to make measurements versus pressure and rates of pressure rise close to application. JH: **Study was entirely on isopropyl nitrate, not NM. Value is analysis of U-tube apparatus and effect of parameters on adiabatic compression. This is an early, but valuable report. Many parameters of adiabatic compression are not considered.**

- -

Abstract: (U) A theoretical analysis has been made of the dynamic behaviour of an apparatus used to reproduce practical conditions in an investigation of the ignition of isopropyl nitrate by the sudden compression of a bubble containing a gas saturated with propyl nitrate vapour. The apparatus consisted of a U-tube containing liquid isopropyl nitrate, the vapour/air mixture being compressed in one arm of the tube when gas pressure was applied suddenly to the surface of the liquid in one other arm.

The peak pressure attainable in the closed arm of the tube, using an inert liquid, is shown to be dependent on a high power of the ratio between the pressure applied to the liquid surface and the initial pressure in the vapour/air space. Thus very high peak pressures result from quite moderate/ applied pressure.

The theoretical peak pressure is found to be independent of the mass of the liquid piston and of the diameter of the tube (which is assumed to be of constant cross-section throughout its length). It is also independent of the length of the vapour/air space.

Theoretical pressure/time and temperature/time curves are derived for several different sets of conditions, in order to study quantitatively the theoretical effects of several variables on the rates of adiabatic pressure and temperature rise in the vapour/air space. It is to be expected that the faster the temperature rise, the more nearly will truly adiabatic conditions be attained in practice, since there will be less opportunity for heat to be dissipated.

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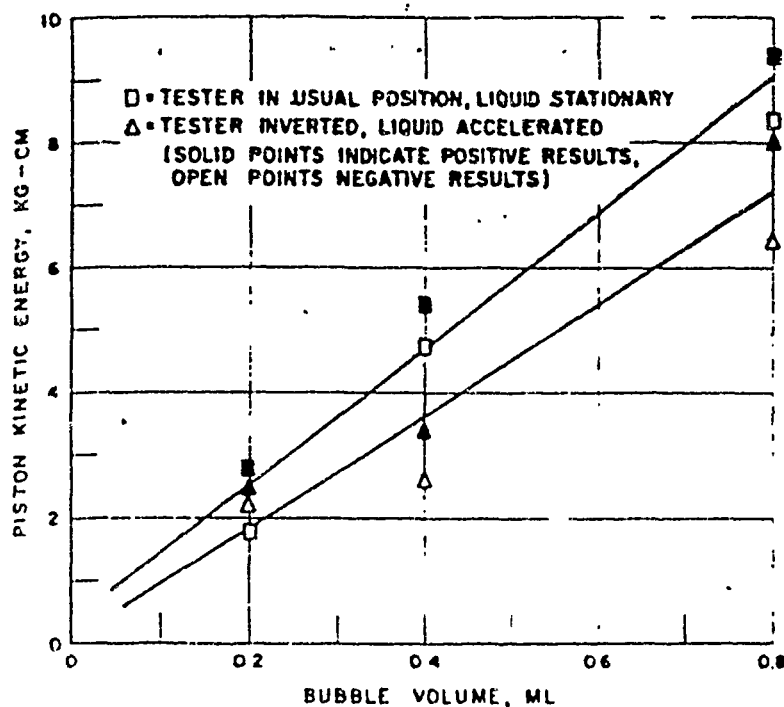
Table of Contents of Report

606/74

"Compression Sensitivity of Monopropellants," G. A. Mead, ARS Journal, pp 192-198, March 1959.

In equipment described, a gas bubble in contact with liquid is subjected to rapid compression by a gas driven piston. Rates of pressurization can be adjusted. Sample chamber volume is about 2.3 mL. Samples from about 0.4 to 1.1 mL liquid volume and from 0.2 to 0.9 mL bubble volume can be tested. Preheating or cooling is possible. Analysis of tester action is provided.

NM was tested in the presence of 0.2, 0.4, and 0.8 mL air bubbles. A positive result represented essentially complete decomposition; negative unaffected. Sensitivity of NM was 10.4 ± 1.7 kg-cm/mL. Figure 10 with data is below.

JH: Here the piston represents the inertia of a liquid column and the pressure pulse generated depends on the time interval in which the pressure peaks. It does not appear possible to extrapolate from this data to the water-hammer ignition of NM. Note that sensitivities are given for other liquids--in particular n-propyl nitrate is 6.7 ± 2, and hydrazine is >144; i.e., NM is at least one order more sensitive than hydrazine and about the same as n-propyl nitrate. JH: Significant regarding other studies.

Figure axes: PISTON KINETIC ENERGY, KG-CM (vertical) vs BUBBLE VOLUME, ML (horizontal)

□ = TESTER IN USUAL POSITION, LIQUID STATIONARY
△ = TESTER INVERTED, LIQUID ACCELERATED
(SOLID POINTS INDICATE POSITIVE RESULTS,
OPEN POINTS NEGATIVE RESULTS)

607/24

"Shock Sensitivity of Liquid Propellants: The Exothermic Decomposition of Isopropyl Nitrate Under Rapid Compression," P. Beeley, P. Gray, and J. F. Griffiths, Seventeenth Symposium (International) on Combustion at University of Leeds, England, August 20-25, 1978.

Goal is to quantify under what conditions of compression gas phase spontaneous ignition may be induced. A rapid compression apparatus is described that acts on gas bubbles. Compression and heating are of the order of milliseconds while dissipation of heat from the compressed gas takes tens of milliseconds so that the time scale for reaction is 1 - 50 msec. The vapor was diluted in N_2, Ar, CO_2, or air or combinations of these. JH: **Note that this measures the role of vapor from the liquid within the gas bubble. Hence it is important as NM has a high vapor pressure. (NM was not studied.)** As compressed gas temperatures increase, pyrolysis increases. In inert gas, only decomposition occurs; in air, oxidation is also important. JH: **Significant regarding nitrogen ullage.** Ignition occurs ony when oxidation augments the decomposition reaction. Recommends: (a) storage with no free volume, (b) inclusion of a volatile polyatome component $(\gamma \rightarrow 1)$ in liquid to enter bubble, (c) fill and store with inert atmosphere. JH: **Avoid adding bubbles or cavitation or impact.**

182

608

"Adiabatic Compression Measurements of Bubble Entrained in Gel Propellant," Neale A. Messina and Larry S. Ingram (PCRL), Princeton Combustion Research Laboratories, Inc., Final Report PCRL-FR-87-007, 30 October 1987.

Describes the PCRL Compression Ignition Sensitivity Tester with which rapid compression was produced in the range of 140 ≤ dp/dt [MPa/msec] ≤ 700 [140 Mpa/msec → 1.4 Kbar/msec → 20,000 psi/millisec].

The equipment allowed for pre-pressurization, so that the level could be found to avoid compression ignition. The tester is shown below. A propellant driven piston provides the controlled compression onto a small volume of the liquid. Provision for loading, introduction of ullage/ bubbles, and measurements of pressure are included. This equipment has been used on liquid propellants to define the safe domain. See other PCRL reports that follow (29/609), (32/610), (35/611), (36/612), (38/613). Other PCRL output may be found in Category 1.
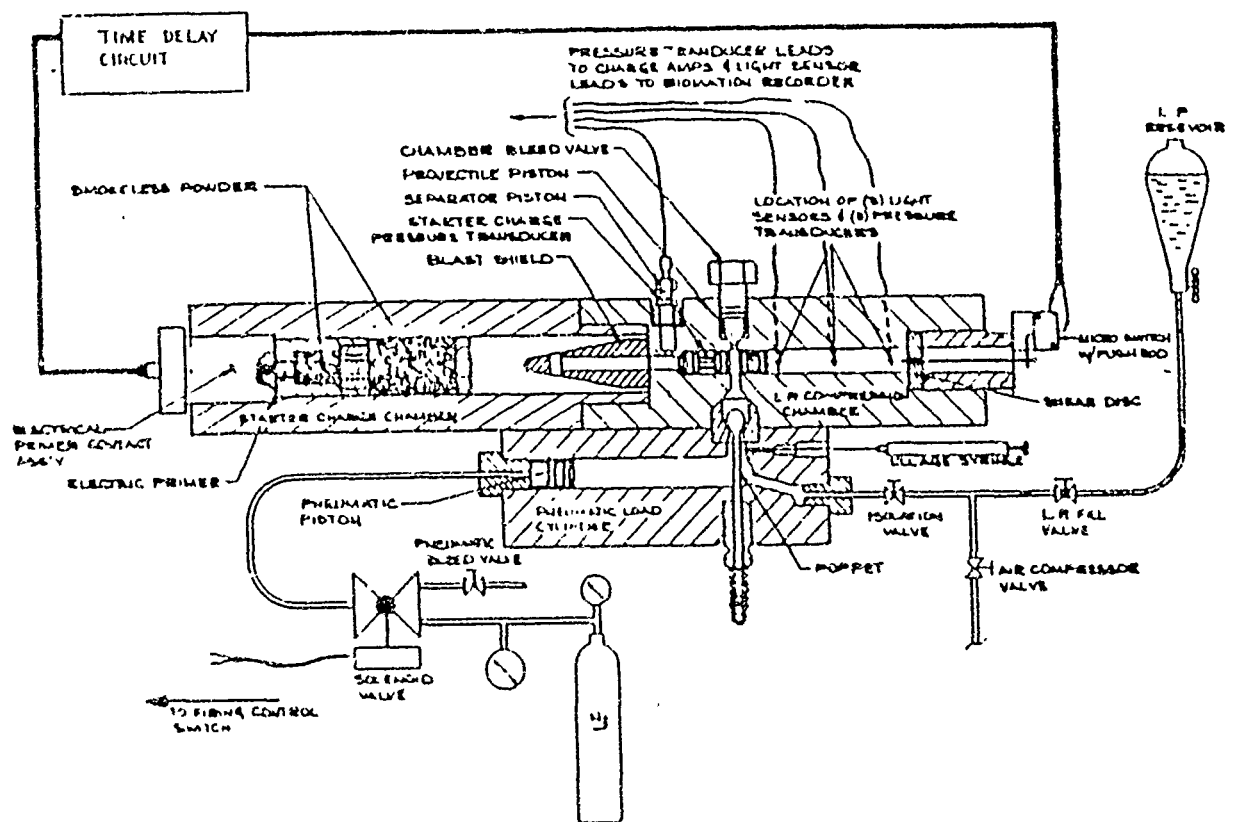
Figure 1. Functional schematic drawing of compression
ignition sensitivity tester.

"Compression Ignition Sensitivity of Liquid Monopropellants at Temperature Extremes," N. A. Messina, L. S. Ingram, and S. A. Traicarico (PCRL), 25th JANNAF Combustion Meeting, October 1988.

For water-based monopropellants with hydroxyl ammonium nitrate as oxidizer (HAN), a systematic increase in sensitivity to compression ignition is indicated by the results as the conditioning temperature is increased from -40°C to 55°C. Residual ullage and cavitation bubbles influence sensitization to compression ignition. Compression Ignition Sensitivity Tester of PCRL used. The kinematic viscosity of HAN increases by three orders of magnitude over temperature range. JH: **How does NM compare with HAN for which viscosity is O(1) at 65°C and O(1000) cSt at -55°C?** At the low temperature extreme, ullage, bubble size and distribution become critically dependent on injection procedures (as large as 0.1 inch). This could have severe consequences on sensitivity to compression ignition. JH: **Note that the effect of temperature depends on which effects dominate; kinetics, vaporization increase with temperature; viscosity decreases with increase in temperature as does compressibility. Gels are very sensitive to compression ignition. Experiments with NM to determine domains in which particular parameters dominate sensitivity for the TEXS fill procedure and stimulus worst case are essential.** Description of tester used does not correspond to the "water-hammer" effect. However, the approach could be altered to simulate both the loading for TEXS and the stimulus for a worst case.

Data for HAN [JH: **Could be different for NM.**] "clearly demonstrate that the compression sensitivity with embedded air bubbles at -40°C is significantly REDUCED compared to test results at ambient temperatures, up to mean liquid pressurization rates of 690 MPa/sec (10 Kpsi/millisec). (It follows that for HAN at the low temperature extreme, kinetics may have dominated.)

"Compression-Ignition Sensitivity Studies of Liquid Monopropellant in a Dynamic-Loading Environment," N. A. Messina, L. S. Ingram, P. E. Camp, and M. Summerfield (PCRL), 16th JANNAF Combustion Meeting, Monterey, CA, September 10-14, 1979, pp 247-284.

Adds to air bubbles, possibility that bubbles may be "simply vapor-filled, formed by cavitation during the filling process." JH: **High vapor pressure of NM makes this an important consideration, particularly at high temperatures.** Whether detonation occurs depends on the quantity of bubbles acting simultaneously. Describes the flow visualization equipment and studies. Shows differences between water and a liquid propellant (not NM). Describes the compression-ignition sensitivity equipment and studies. Shows need for adequately large bubbles to produce reaction under conditions of pressure profile and collapse rate. For slow kinetics and tiny bubbles, transport prevents runaway reaction or ignition. JH: **Provides the limited experimental data to support the PCRL theoretical treatment of bubble collapse.**

611/35/412

"Sensitivity of Liquid Monopropellants to Compression Ignition: A Progress Report," N. A. Messina, L. S. Ingram, and M. Summerfield (PCRL), 19th JANNAF Combustion Meeting, Greenbelt, MD, October 4-7, 1982, Vol I, pp 521-533.

Bubbles may be brought into the chamber during loading or may be formed by cavitation during the filling process. Visualization was done for a piston ram system. The liquid is somewhat compressible, and the compression wave propagates through the column with a finite velocity, stagnating the fluid to meet boundary condition. The pressure pulse collapses cavities producing hot spots. "Water hammer" peaks of 1000 psi and pressurization rates of 10 Kpsi/ msec are obtained. However, for those liquids considered, ignition has not occurred. Propellant was not re-used because of bubble content and possible change in rheological properties. Used a compression ignition sensitivity tester to do tests versus bubbles in liquid. Found a finite induction time needed for pressure generation due to gas evolution, and runaway reaction always occurred well afterward. Confinement time under pressure is thus a factor. **JH: Not for NM. Parallel studies for TEXS are needed.**

612/36

"The Role of Physical Properties in Dynamic Loading Processes and Bubble Collapse of Liquid Monopropellants for LPG Application," N. A. Messina, H. H. Tseng, L. S. Ingram, and M. Summerfield (PCRL), 21st JANNAF Combustion Meeting, Laurel, MD, October 1-4, 1984, Vol II, pp 515-527.

The real fluid effects that are important in bubble collapse dynamics are vapor pressure, density, viscosity, surface tension, liquid compressibility. Modifies Rayleigh equation. Finds viscosity reduces rate of bubble collapse. Surface tension effects always acts opposite to gas pressure and vapor pressure effects. Surface tension dominates for small bubbles, but these are not important for ignition by adiabatic compression. Provides methods for measurement of the relevant physical properties.

JH: This is not for NM. A study such as this for NM is required, with real property relevance for TEXS dynamic range and temperatures of military interest used to set domain of interest.

613/38

"Sensitivity of Liquid Monopropellants to Compression Ignition," N. A. Messina, L. S. Ingram, M. Summerfield (PCRL), 18th JANNAF Combustion Meeting, Vol II, pp 269-287, 1981.

Identifies the problem as defining the safe domain of operation. Provides information on transport visualization chamber and pneumatic load cylinder. Presents test considerations for determining by compression igni-

tion sensitivity test the threshold conditions for runaway reaction. Summarizes results as a three dimensional plot based on the critical parameters—pressurization rate, volumetric air ullage, or distributed with particular bubble profile and injection pressure.

JH: Although not done for NM, the framework for consideration would be useful for TEXS. However, the domain of parameters is different for TEXS.

614/42

"Nitromethane Based Monopropellants," U.S. Air Force Technical Report AFRPL-TR-81-17, 88D176-D183, May 1981.

U-tube adiabatic compression test described. Driving pressure of nitrogen acts on 2 mL of liquid via a rapid opening valve (90% open in 1 msec—for 500 psig rate is 5.2 x 10^5 psi/sec). Up and down procedure used with positive result, one in which the stainless steel tube is ruptured by explosive decomposition (severed or fragments torn out). Negative: intact or split. For NM Figure 1 gives details of apparatus. Propellant sample is in $\frac{1}{4}$ inch o.d. tube at base of U test section. Approximately 5 $\frac{1}{2}$ inch height (on side away from accumulator) of tube is region in which nitrogen gas is compressed against plug.

Driving Pressure (psig)	750	700	650	600	550	500	450
Pressure Ratio	52.0	48.6	45.2	41.8	38.4	35.0	31.6
Positive Results	2	2	1	1	1	1	0
Negative Results	3	2	2	2	1	2	10

JH: No included bubble. Small diameter, probably no froth. Small surface area of liquid in contact with compressed gas, metal surround. Not clear what is pressure and thermal loading of NM versus time.

615/45

Nitromethane TEXS System, Safety Assessment Report (SAR), June 1988, ANGUS Chemical Company.

Appendix B quotes (42) and (614) giving test design for U-tube adiabatic compression test with results—includes ether tests. Appendix C responds to question of hazard of self detonation during pumping—has analysis. Pages 14 and 15 of separate safety assessment report discusses in 4.3 sensitivity to adiabatic compression.

Appendix B gives results for NM and details of U-tube apparatus taken from AFRPL-TR-81-17 dated May 1981. [See summary of (42).] Also had liquid drop weight tests (ASTM-D-2540) and thermal stability test (Liquid Propellant Test Methods, Test No. 6). With a 4 kg weight disc, rupture occurs with

water at 190.7 (50%) kg-cm and for NM > 160 kg-cm, i.e., greater than 80% of water value. Reference n-propylnitrate burst disc using a 2 kg weight of 7 kg-cm. Therefore, NM liquid insensitive. Thermal stability test shows major exotherm at 570°F and burst disc rupture which requires 5300 psi at 685°F.

Appendix C gives math analysis for converting the flow energy to potential energy in the form of a compressed elastic medium in a completely rigid pipe with the piston coming to a complete sudden halt (no bounce). Finds must exceed 785°F for 100 microseconds to have potential for self detonation. Then does water hammer calculation for 4 x 25 gal/min of 8.5 psi as initial flow. Gets 100 psia and T = 428°F which does not meet minimum for detonation. **JH: See (408).**

JH: This calculation ignores bubbles and froth consistent with ANGUS position that no air enters. An error regarding air adiabatically compressed above that threshold could be catastrophic.

616/52

"Explosive Decomposition of Hydrazine by Rapid Compression of Gas Ullages," D. Baker, et al., 1988 JANNAF Safety and Environmental Protection Subcommittee Meeting, Chemical Propulsion Information Agency, May 1988.

Water hammer pressures (hydrodynamic surge pressures) are much greater than the push pressures accelerating the liquid. For example, a surge pressure of 3600 psi resulted for water accelerated with a push pressure of 200 psi into a line pressurized with nitrogen at 0.1 psia. **JH: For TEXS, push pressure corresponds to pump action; surge corresponds to pressure when fluid is dead-headed (stagnated).** Experiments were done for hydrazine, accelerated, and rapidly brought to rest and compared with results for water. Test system described. As surge pressure increased, a condition was reached where significant decomposition occurred, raising the pressure above that for water. **JH: Ullage pressures could exist in drums at higher temperature due to NM expansion and vaporization.** Ullage gas necessary to initiate decomposition. However, as the pressure of the ullage gas increased, the hydrodynamic surge pressure decreased and eventually reached a level at which hydrazine decomposition could not be initiated. **JH: Gas at higher pressures acts as a cushion in bringing the liquid to rest, so that lesser pressures are generated in the rearward compression wave in the liquid.**

Tests were performed in which an 8 inch column of liquid was accelerated by a 500 psi push pressure into a 15 inch long glass chamber pressurized with nitrogen at 12.4 psi. A video camera showed leading region of cloudiness believed to be a froth created by Taylor instabilities at the liquid-gas interface, resulting in Helmholtz mixing of gas and liquid (gives ref.). After impact at the dead head, the froth was compressed by the liquid column. Froth maximizes surface, and under compression heat transfer is very rapid leading to rapid thermal runaway. Container rupture occurred for hydrazine, not for water.

Has excellent review for hydrazine with references, some of which may be extrapolatable to NM.

617/57

"Compression Ignition Studies of a Liquid Monopropellant," A. H. Mitchell and H. A. Kirshner, AJAA Journal, 1, 9, pp 2083-2087, September 1968.

Equipment provided control of compression rate, piston travel, velocity, and bounce. Pressure in liquid measured, and high speed photography included. Figures and description given. Piston velocities 5.7, 13.4, 17.3 fps showed more liquid agitation at 17.3 than the lower rates. Measured deviation from pressure for adiabatic compression. Decrease in pressure increased with higher compression ratios attributed to increased cooling of the compressed gas phase with increasing compression ratio due to higher temperature gradients at the turbulent vapor-liquid interface. **JH: Shows need to consider the interface between liquid and gas/vapor in a rapid compression.** Studied ethyl and n-propyl nitrate, not NM. Horizontal compressions appear to give ignition at lower compression ratios for high piston velocities. (Compression ratios > 100:1, 100:1, 80:1, 80:1 for 5.7 13.4, 17.3 fps.) Ignitions at high piston velocities were more violent as a result of the extensive liquid-gas interface obtained. **JH: This is early indication of role of froth.** [See (50)-(53).]

618

"Classification of Liquid Gun Propellants and Raw Materials for Transportation and Storage," William J. Cruice, Hazards Research Corporation, Contract Report ARBRL-CR-00454, May 1981.

This report is concerned with modifying for liquids the tests normally used to classify solids according to the military explosive classification system as described in Department of the Army Technical Bulletin Cl, TB 700-2. The tests considered were: Trauzl thermal stability, impact, detonation velocity, card gap, long term thermal stability, flash point, auto-ignition temperature, deflagration potential, and thermal stability scan. The tests are described and were applied to liquid propellants (for liquid propellant gun). Results are given and recommendations as to classification provided. NM was not included.

On page 20 the importance of confinement as part of classification is noted as applying in a case "for lowest possible confinement where fire exposure will definitely result in very rapid failure of confining vessel and venting of products. Any shipping container conformation should be subjected to fire exposure tests before use, as degree of confinement may well alter the recommended classification." **JH: Applies for NM and 50 gallon drums.**

188

619

"Function and Safety Tests of NOS-365 Monopropellant," H. Dean Mallory (NWC), Naval Weapons Center, NWC TP-5940, April 1977.

Compares NOS-365 with a reaction time for the steady state detonation zone in excess of 10 microseconds with NM whose reaction time is 22 nanoseconds. **JH: This is for pure NM in high velocity detonation. For LVD it is orders of magnitude longer.** Suggest that long reaction time corresponds to long run-up time which can be critically affected by other features, e.g., confinement. Describes a test, unique to NWC, called the "Impedance Mirror Test." This test is used to measure detonation reaction zone differences with a streak camera. NM was checked down to liquid nitrogen temperatures with no affect on reaction time. A "tube test" was described in which the liquid is confined in a 0.9 m long tube with a 25 mm bore and 25 mm thick wall to study run-up. Spill tests on desert soil are described. **JH: Should be done for NM.** Spills onto soil and onto rusty iron at temperatures up to 77°C. Fume-off reactions occurred for NOS 365 propellant as low as 45°C after a 30 minute delay and on soil after about 5 seconds of contact. Soil may catalyze reaction due to transition metal oxides present in soil. **JH: NM spills will occur, source for contamination reaction.**

620

"Development of a Simple Stability Test for Monopropellants Utilizing a Detonating Cup and Heavy Confinement," Richard S. Egly and Quentin R. Jeffries, Western States Section Combustion Institute, Paper WSCD 65, 35, 1965.

The height to which a weight is thrown when a cap is detonated is taken as a measure of energy liberated. Using 4 mL, NM provides 48 feet, whereas hydrazine is 39 feet, and n-propylnitrate 29 feet. Results are stated to be indicative of adiabatic compression hazard based on the belief that the "air around the sample must develop the temperatures and pressures necessary to ignite and deflagrate the NM." Details of the development of the test are given. The order of sensitivity with this test is in contradiction to that obtained with the JANNAF Adiabatic Compression Test, Liquid Propellant Test Method. The latter uses mechanical compression by a gas driven piston **(JH: This is PCRL approach.)** so that pressure and temperature build-up are much slower than that initiated by a detonating cap. **JH: It really depends on what one is trying to simulate with the test. For hydraulic hammer, inert loading at the rates supplied by the piston seems more appropriate than a detonating cap.**
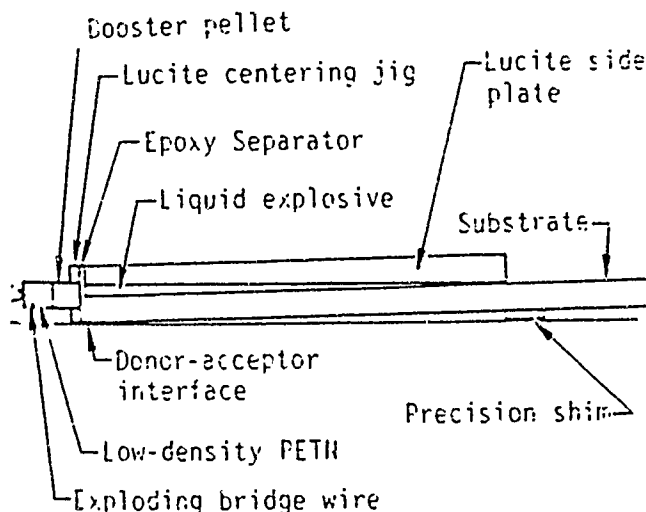
"Physical, Stability, and Sensitivity Properties of Liquid Explosives," K. Scribner, R. Elson, R. Fyfe, J. P. Cramer (LLNL), Sixth Symposium (International) on Detonation, August 24-27, 1976, ACR-221, ONR, Dept. of the Navy, pp 466-474.

Results do not include those for NM. Concern was thin films of the liquid forming on equipment. Developed a low velocity detonation screening test and determined the minimum liquid film thickness below which detonation did not propagate. The test consists of a wedge of liquid initiated at the thick end as shown in sketch. The aluminum base serves as a witness plate and is examined afterward for signs of the various reactions that occurred during the test.

Detonation failures:

Thickness (mm)

	HVD	LVD
NG	0.6	0
FEFO	0.9	0

Therefore LVD always propagated here.

Labels: Booster pellet, Lucite centering jig, Lucite side plate, Epoxy Separator, Liquid explosive, Substrate, Donor-acceptor interface, Precision shim, Low-density PETN, Exploding bridge wire

"Impact Sensitivity Test for Liquid Explosives," Bureau of Explosives Design, ICC requirements for Class A Desensitized Liquid Explosives in accordance with para 73.53 of ICC Tariff No. 10.

Describes the procedure and design of test. It consists of an anvil-striker assembly that acts by dropping an (ght pound weight from a height of 15 inches or less onto a one drop from a 25 mL popette (about 0.25 g) that is confined in a cup. JH: The equipment would have to be seen at the Burrau of Explosives and more details obtained if it became necessary to run this test.

The Shock Sensitivity of Explosive Films," R. Watson, J. Ribovich, F. C. Gibson (BuMines), Pyrodynamics, 6, pp 391-51, 1968.

Two dimensional analog of card gap test to test shock sensitivity of thin films of liquid explosives is described. Qualitative characteristics of the low-velocity detonation in films are found to closely resemble those of LVD, in that fluid cavitation is involved. Uses a velocity probe in the film to follow run-up and propagation velocity. Did not test NM. Mostly

tested NG-EGDN and with triacetin. Donor was 50 grams of tetryl. Tray was 12 in. x 12 in. x 1 in. with 1/2 in. thick base plate. Measured films from 1/32 in. to 1/8 in. thick. Figure 8 shows that at 1/8 in. thick film initiation threshold is about 1/2 that for a 1 in. diameter column. "The important practical results are the findings that the sensitivity of the thin films to LVD is alarmingly higher than the sensitivity of the same system to the initiation of HVD." ". . . an incident peak pressure of 30 Kbar is required for initiation of HVD in a 1/8 in. thick film of NG-EGDN, whereas a pressure of only 1.5 Kbar will initiate LVD in the same thickness." ". . . serves to emphasize the hazards associated with accidental spillage and processing equipment leakage." **JH: This hazard should be evaluated for films of cavitated, contaminated hot NM.**

624

"A Compilation of Hazards Test Data for Propellants and Related Materials," Radford Army Ammunition Plant, Hercules Incorporated, Final Engineering Report (on PE-489), RAD 100.10, selected pages.

NM not included. Extensive results on NG. Describes friction test, impact test, and thin film propagation test [see also (621)] and gives results for these in terms of threshold initiation level.

The friction test slides an anvil at a specified velocity below a stationary wheel resting on the specimen with an assigned force. The impact sensitivity test uses a guided 2 kg weight acting on an intermediate hammer that rests on the sample placed on an vil with a force gage. The thin film propagation test uses a falling weight for initiation and resistance wire probe in the liquid to follow run-up and failure in a sample of variable depth and width.

JH: Thin film propagation for NM would be of interest for TEXS regarding hazard of spills, particularly if contaminated by soil or objects contacted. See (619).

625

"Large Scale Drop and Projectile Impact Sensitivity Tests of Nitromethane," R. T. Keyes (R. S. Egly involved), Intermountain Research and Engineering Co., Inc., Report No. 11-NM2, July 16, 1958. PA U134842

Report describes large-scale tests regarding susceptibility to detonation by drop and projectile impact.

Abstract: It was found impossible to detonate drums of nitromethane (NM) dropped 50 feet onto a steel plate with protruding sharp pointed pins, onto a steel plate without protruding pins, or onto other drums of NM. Furthermore, no detonations resulted when a 100 pound weight with a sharp pointed nose, one with a rounded nose, and one with a flat nose were dropped 50 feet onto 55 gallon drums of NM.

A 50 caliber (45 gram) high velocity bullet impact at 3600 ft/sec was found insufficient to detonate a 55 gallon drum of NM without the use of steel plates to stop the bullet in the NM. By means of a combination of aeration of NM, steel plate backing and front steel plate it was possible on one occasion to detonate the NM and on another to cause it to ignite and burn without detonation. Several attempts to duplicate detonation, however, resulted in failure.

No detonations were obtained in the bullet impact test using the 50 caliber, 45 gram, 3600 ft/sec bullet impact test with the nitromethane at 83° and 92°C and the drum back and front surfaced with heavy steel plates.

A 55 gallon drum of NM was detonated by a 1/2 in. thick, 6 in. x 6 in. steel plate hurled at the NM by a 10 in. (d) x 10 in. (L) cast 50/50 pentolite charge at a distance of 25 feet.

JH: Note that the one occasion that detonation occurred included aeration of NM. These tests simulated possible accidents in handling and shipping and vulnerability to certain enemy attacks. To the extent that these simulations correspond to the real situations, the results on NM are very encouraging. The problems are the latter and whether the worst case has been included. In the absence of laboratory tests preceding the simulation tests, one does not know the effect of various aeration profiles, or of temperature, or of possible contamination or combinations. It is clear though from these tests that it would take some set of special circumstances to cause an important hazard to exist. Since the consequences of an explosion would be disastrous, it is important to identify the worst case and then do additional simulation tests for it.

626

"Sensitivity and Desensitization of Nitroglycerin," C. Boyars (NSWC), Second Symposium on Chemical Problems Connected with the Stability of Explosives, edited by J. Hansson, Chairman, Section for Detonation and Combustion, Tyringe, Sweden, May 1970.

A standard drop-weight test apparatus was instrumented for pressure-time and photography to study impact initiation and explosion process in NG, not NM. The probability of explosions "is consistent with quasi-adiabatic compression of air bubbles as a step in the mechanism of initiation. Photography shows " . . . heat transfer accelerated by spray formation, an induction period and ignition starting in hot spots at the site of the bubble." Increasing viscosity decreases sensitivity "by eliminating spray formation (Munroe jets) in the bubbles." Details are given for Olin-Mathieson drop weight tester designed specifically for liquid samples and which includes a controlled gas volume. JH: Note the importance of this feature regarding ullage and bubbles. Note also spray formation mentioned which corresponds to froth formation in propagation. See 50-53, and 57.

627

"Desensitization of Nitroglycerin: Viscosity Effects," C. Boyars (NSWC), Combustion and Flame, 13, pp 439-440, 1969.

This paper refers to the previous one for all detail (626). Asserts that, "Accidental explosions in the handling of NG are presumed to be initiated frequently by a process similar to that in Olin-Mathieson Tester" spray formation in bubbles under impact. Recommends increasing viscosity of liquid and shows that it does reduce impact sensitivity. JH: These results, if valid for NM, would indicate a fundamental value in increasing viscosity and an inherent advantage of gelled materials if all other factors are equal as a means to reduce hazard.

628

"Drop-Weight Impact Sensitivity of Explosives," Carl Boyars and Donald Levine (NSWC), Pyrodynamics, 6, pp 53-77, 1968.

This is a chronological and historical review of the technical aspects of impact sensitivity testing of explosives equipment. It is the major reference for this subject and includes an annotated bibliography. JH: Reading this paper is a preliminary and essential prerequisite for doing any work on equipment for impact sensitivity. The paper refers also to the role of energy concentrators (hot spots, Munroe jets, bubbles, etc.) in reducing sensitivity thresholds. However, such information is found in many other references. There is a section on liquid explosives (starts p 61) that stresses microjets in bubbles. It is also recognized therein that the vapor within the bubble is important. "The higher probability of explosion was attributed to the exothermic decomposition of the vapor" of NG (no info for NM) and also "to oxygen content of gas used." JH: NM has a high vapor pressure. Air contains oxygen, a nitrogen blanket removes air at surface, and in solution re later cavitation into bubbles.

629

"Measurement of Impact Sensitivity of Liquid Explosives and Monopropellants," Donald Levine and Carl Boyars (NSWC), Advanced Propellant Chemistry (symposium sponsored by Division of Fuel Chemistry, ACS), Advances in Chemistry Series, 54, Robert F. Gould, editor, pp 261-278, 1966.

This paper is an earlier version of (626). It provides more detail on the equipment used for studies of impact sensitivity of NG. No work included on NM.

630

"The Sensitivity of Nitroglycerin to Impact," D. Levine and C. Boyars (NSWC), Combustion and Flame, 9, pp 131-140, 1965.

This is the earliest paper on the work on impact sensitivity of liquid explosives, in particular NG. This series of papers have the same authors together or Carl Boyars alone. The set consists of (626)-1970, (627)-1969, (628)-1968, (629)-1966, and (630)-1965. The comprehensive introduction to the subject and the work of others is in (628). The use of the equipment in its final form, and the exposition of results, is best started with (626) with earlier papers used for more detail on equipment and procedures.

631

"Bureau of Mines Internal Ignition and Gap Tests," R. J. Mainiero and J. E. Hay, Pittsburgh Research Center Internal Report No. 4521, April 1985.

A description is given of a pipe bomb used for an internal ignition test. The explosive in the pipe bomb is subjected to the action of a centrally located black powder (20 g) igniter. A positive result occurs if either the pipe or at least one end is fragmented into at least two distinct pieces. A negative result corresponds to just split open or caps blown off. Therefore, it is a rough test of rapid burning versus detonation.

The BuMines Gap Test for liquids with a bubble source included is described and shown in Figure 3.

Results for these two tests are given in Table 1 for many energetic materials but not for NM.

JH: Suggest looking at Figure 3 for possible use of bubbles source.

632

"Chemical Sensitization of .litro Compounds," M. D. Cook and P. J. Haskins (RARDE, GB), Combustion and Detonation Phenomena, 19th International Annual Conference, June 29 - July 1, 1988, Karlsruhe, Germany, pp 85-1 to 85-8.

Provides an up-to-date descriptoin of the RARDE Large Scale Gap Test applied to liquids and specifically to NM. For pure NM a gap value of 13 mm of Perspex (= Lucite = Plexiglas) was found to be the threshold. The change in gap values for additives in NM is given. Also to investigate the role of aci-ion suggested by Engelke (LANL) [see (70)], added amines to series that were different--nitroethane, 2-nitropropane, 2 methyl-2 nitropropane through all nitroalkanes. Uses this info and goes on to discuss the mechanism of sensitization of NM. Concludes that "the results of our experiments are not consistent with the hypothesis that the sensitization of nitro compounds is due to the increase in concentration of aci-ions." The tentative alternate explanation is "due to the ability to form complexes with increased reactivity." Further studies are underway. JH: This same reference was also

reviewed as (71) for pertinence to Category 1. Both reviews can be looked at for a more complete description.

633

"Thermal Reaction Initiation of Liquid Propellants," Nathan Klein (BRL), Combustion and Detonation Phenomena, 19th International Annual Conference, June 29 - July 1, 1988, Karlsruhe, Germany, pp 17-1 to 17-11.

Devoted to HAN (aqueous mixtures of the nitrate salts of hydroxylamine) and an aliphatic amine (AAN). Discusses use of an adiabatic calorimeter as an experimental method to determine stability and study ignition and combustion. Describes the pressure vessel of ANSI 316 stainless steel used to prevent interaction with material under test. **JH: This may not be suitable for NM according to reference data on NM.** Had problems and changed to tantalum. Modifications to commercial equipment are given. No tests done on NM.

634

"Explosive Properties of Nitromethane," Louis Medard, Memorial Des Poudres Tome XXXIII, pp 125-135, In French (translation), 1951.

Note that this was written in 1951 and test methods have been improved since then. Tests described for sensitivity to initiation, transmission to detonation, specific work, sensitivity to shock and high temperature, and detonation velocity. "Care was taken not to leave any air bubbles in the tube" and concluded that NM is not very sensitive to initiation. **JH: Certainly true for pure NM.** The transmission test shown in Figure 1 is unique and in modern parlance one would say transfer occurs if the diameter exceeds the critical diameter.

An absorbent earth was added to NM (of the silica gel type) until a mixture was obtained which did not exude when pressed with the fingers. This mixture contained 40 parts of absorbent per 60 parts of liquid. It had a density of about one, and in two trials the detonator did not initiate the mixture. **JH: But the same detonator used with NM in the same confinement also did NOT initiate the NM. Therefore, no conclusion is possible.** An apparatus to study sensitivity of NM vapor at high temperatures is shown in Figure 2. At 70°C vapor pressure is 258 mm of Hg. Incandescent filament causes explosion but test tube and liquid remain intact. **JH: No transfer, but for analagous conditions, the vapors of methyl nitrate or those of the mixture of TNM and toluene result in detonation of the liquid phase. There is an important suggestion here that the hazard of explosion of NM be tested and also the conditions under which this would cause the detonation of liquid NM in contact be ascertained. Vapor in ullage is a case-in-point and presence of nitrogen may be important.**

Flast point of NM is given as "near 35°C?"

635/13/301

"Initiation and Growth of Detonation in Liquid Explosives, F. C. Gibson, C. R. Summers, C. M. Mason, and R. W. Van Dolah (BuMines), Third Symposium on Detonation, pp 436-454, 1960.

Begins with a summary with reference citations of possible alternate mechanisms to adiabatic compression of contained gas. Did initiation and growth studies in liquid explosives (with test configuration shown in Fig. 1) by shock excitation. Configurations and wall materials were changed in a form of card gap test. Proposes mechanism for initiation of detonation in liquid explosives as cavitation established by shock excitation, possibly with additional heating of the liquid provided by shear forces resulting from differential particle velocities in the liquid and between the liquid and container walls. For a high intensity stimulus, gas bubbles will be formed from the dissolved gases which may first exist as small invisible bubbles of microscopic dimensions. These bubbles, finely dispersed throughout the liquid, constitute weak points as the tensile strength is determined by the largest bubble present. In addition, impurities such as dust particles provide nuclei as do small imperfections in the wall. During cavitation small bubbles may coalesce into larger bubbles of a size sufficient for compression to result in adiabatic heating. Any decomposition of the vapor or droplets in the bubbles which results in the production of gas also results in an increase in bubble size. The time required for the foci to grow through coalescence and reaction may well account for the long delays observed in this initiation process. JH: The sequence describing the role of bubble formation and growth is equally applicable to the point where a stimulus acts on the larger bubbles or created ullage. Whether ignition occurs then depends on the profile of the stimulus and the reactivity of the vapor and liquid as well as the thermal conductivity of both gas, vapor, and liquid and mechanical properties that modulate the adiabatic compression into oscillations at particular rates of compression. For the low velocity detonation model in which the wall carries a precursor shock producing cavitation, the speed of disturbance in the wall material and as a pipe should be established by literature or experiment. This must be compared with velocity in NM and impedances of NM and wall to determine whether a precursor could exist. For performance, one would think that high velocity detonation is desired. However, for cratering, it may very well be that low velocity detonation would be more effective. The selection will depend (if low velocity detonation is feasible) on the mode of initiation. [See (14).]

636/14/303

"Detonations in Liquid Explosives - The Low Velocity Regime," R. W. Watson, C. R. Summers, F. C. Gibson, and R. W. Van Dolah (BuMines), Fourth Symposium (International) on Detonation, pp 117-125, 1965.

Begins with a summary with reference citations to earlier work on low velocity detonation. Figure 1 provides the geometry for study of low velocity detonations. "Interest in the low velocity phenomenon has developed following recognition that these abnormal detonations play an important part in characterizing the hazards of liquid explosive systems, as demonstrated by

the too frequent accidents that have occurred in NG and liquid monopropellant facilities from relatively mild stimuli." LVD "can be initiated by pressures one or two orders of magnitude less than that required for HVD." Concludes "that perturbations of the liquid resulting from precursor wall waves exert a strong influence on the subsequent reactions." For an observer that moves with the reaction, the sequence of events can be visualized as: (a) undisturbed liquid compressed by bow waves derived from the precursor wave in the wall; (b) the compressed fluid begins to move outward where the wall moves outward; (c) liquid cavitates; (d) cavities grow until encounter shocks near reaction zone; (e) cavities collapse, generating high pressures and associated temperatures that are adequate to initiate chemical reaction. Model for LVD requires that shock velocity in wall be greater than in liquid for stable propagation. **JH: Note that (b) depends on nature of wall; plastic wall moves out more and faster than steel. Also, need wall and liquid properties to support this mechanism.**

Experiments using air-filled hemispherical cavities located on the free surface of fluids, as well as air-filled bubbles in a bulk of liquid explosive, indicate that liquid micojetting may be responsible for the initiation of reaction within the cavities. **JH: For microjetting to be a viable mechanism, a shock must act on a bubble. Mader's work (314) used 95 Kbars; even two orders lower 0.95 Kbars, 950 atmospheres, would be far above pressures to be encountered by any water hammer scenario. This study used a tetryl donor acting through Plexiglas to produce a weak shock.** Authors cite their work in R. W. Watson and F. C. Gibson's, "Jets from Imploding Bubbles," Nature, 204, 4965, pp 1296-1297, 1964. There they used a tetryl donor acting through 0.75-inch thick aluminum on a bubble in liquid. The pressure that acted was 10 Kbar. The pressure at jet impact was estimated as 100 Kbar. **JH: Again note microjetting coincides with at least a weak shock, but could be important for transition process from LVD to HVD. LVD or HVD depends on initiating stimulus.**

637/15/304

BuMines Quarterly Reports on Sensitivity of Propellant Systems, January 1, 1966 – March 31, 1966, Quarter #6, "Initiation Mechanisms," and April 1, 1966 – June 30, 1966, Quarter #7, "Theoretical Studies on Bubble Compression and Growth," PA U110 487.

Input pressure acting on bubble 1.5 Kbars, 1500 atmospheres. Found threshold for EGDN liquid with bubbles containing air, CO_2, and Argon. For latter threshold lower than 1.5 Kbars. A column of gas bubbles is injected into the liquid by means of a No. 27 hypodermic needle having an inside diameter of 0.007 inch. The gas bubble experiments show a trend toward higher sensitivity as the ratio of specific heats of the included gas is increased, which supports the contention that the heat generated by the compression of the bubble contents may be responsible for the reaction. **JH: This conclusion is based on a simple model of bubble collapse and should be compared with the more comprehensive treatment of PCRL authors (32)(33). Also, see (68) regarding gas diffusivity.**

The observation that some degree of reaction takes place below the thresholds suggests that the initial reaction takes place in the vapor and/or droplet field within the bubble. If the rate of release is great enough, the surface of the cavity could then be ignited resulting in a propagating reaction. The reaction would fail to propagate if the energy released was inadequate to compensate for the losses resulting from the heat transferred to the surrounding fluid and the work done in establishing the flow field around the expanding bubble. JH: **This balance is why the rate of bubble collapse (or oscillation) assumes so dominant a role.** Figure 3 shows the arrangement for studying initiation of liquids containing bubbles.

The second progress report provides a theoretical study on bubble expansion due to internal burning. Liquid is assumed incompressible—spherical symmetry used. Designates a volume consumption rate per unit area of bubble surface, u_c, and average molecular weight of products, w, and assumes both ideal gas EOS and isothermal behavior of uniform products within. Then treats special case of stability of bubble expansion versus five different consumption rate expressions. Finds that for greater than a 1.5 power in rate law stable expansion will occur. For LVD, consumption rates are far higher than studied here. For such high rates, expect that turbulence/breakup of liquid would accelerate consumption and lead to LVD to HVD transition. Recognizes that at high pressures, factors neglected or assumptions made would not be valid. JH: **Interesting approach to important role of kinetics in ignition and growth. Vapor concentration at high temperatures would alter burning rate.**

638/16/308

"Initiation of Detonation in Insensitive Liquid Explosives by Low-Amplitude Compression Waves," J. E. Hay and R. W. Watson (BuMines), Sixth Symposium (International) on Detonation, pp 115-123, 1976.

An experiment devised to simulate the development of explosive reaction in a large mass of cavitated liquid is described in which a massive steel piston is propelled into a container (diameter 10 cm) filled with a liquid explosive into which bubbles have been introduced. In this experiment, transition to "detonation" has resulted using nitromethane and other marginally detonable liquids at initial piston velocities of 24 to 90 meters per second. With further increase in scale size, abrupt accelerations of the order of those occurring in transport may suffice to produce explosion. JH: **This is closest to TEXS application.**

A mathematical model is described by which the hazard potential of deflagration-to-detonation transition in large masses of a reactive liquid subjected to cavitating conditions and pressure surges can be assessed from buring rate data or from small-scale experiments such as that described.

Begins with a critique of Chaiken (18) whose results tend to indicate that the possibility of LVD in NM is marginal. Attributes his result to the large value of the calculated cavitation rate constant which leads to decoupling of cavitation and reaction processes. Describes test for development of explosive reactions in liquids by weak stimulus (<1 Kbar). Projectile

tile driven by compressed air moves down a steel barrel (10.2 cm i.d., 3.3 m long). The minimum criterion for explosion is cylinder unfolded or in pieces, significant blast, and complete consumption of the liquid. Bubble field in liquid with diameters in the range of 0.05 to 0.2 cm and density 0.5 to 10 cm^3. In earlier work it was found that for NM initiations could not be obtained with the highest velocity when only one or a few large bubbles were present. The impact of the projectile on NM at the highest velocity produces about 2.5 Kbars. The threshold velocity for NM was 24 ± m/sec. Comparison with other liquids, on the basis of thresholds and literature burning rates, suggest that those systems that have burning rates less than about 0.13 cm/sec at 11 MPa do not seem to explode at the highest velocity of this test, and those with rates substantially greater exploded at lower impact velocities. Value for NM = 0.27. **JH: NM does explode at 24 ± 2 m/sec if bubble profile is present.**

Presents a simplified model with incompressible liquid (considers value for less than a few Kbars), spherical symmetry, Abel equation of state, isothermal expansion, and some simplifying mathematical assumptions. Derives bubble pressure versus time as a function of parameters (Fig. 2). Finds development of explosive reaction is very sensitive to the burning rate parameter, somewhat sensitive to bubble dimensions and density and importantly with scaling upward. In Discussion, R. T. Solouklin suggests that effect of assymmetric collapse must also be taken into account.

639/17/302

"The Effect of Physical and Chemical Properties on the Sensitivity of Liquid Explosives," J. E. Hay, J. Ribovich, F. H. Scott, and F. C. Gibson (BuMines), Fourth Symposium (International) on Detonation, pp 412-425, 1965.

Some LVD's have a steady propagation rate well above sonic velocity in the explosive and produce well-defined shocks of the order of 5-10 Kbars. Other LVD's have a fluctuating propagation velocity well below the sonic velocity and produce pressurs of the order of 2 Kbars or less but no clearly discernible shock wave.

Bulk temperature rise inadequate, hence energy concentrators required. Each element of the liquid must be subjected to two distinct stimuli: a rarefaction which cavitates the liquid, and a shock which causes cavity collapse. **JH: The mechanism applies to local ignition by "water-hammer" compression which can then transform to LVD and possibly to HVD.**

Describes card-gap test for liquids including resistance type probe. Gives results for NM. At 25°C used schedule 40 steel pipe of normal size 1 ½ to 4 inches with 16 inch length except for 4 inch was 72 inches long. Variations of donor and temperature. Results were ambiguous as shown in Table 2. No appreciable temperature effect was found. Threshold gaps corresponded to shock pressures in NM of about 11.5 Kbars.

JH: In later papers, the role of the wall in producing a precursor cavitation wave in the liquid was defined. However, data is valid in showing threshold from non-initiation (NI) as 11.5 Kbars for shock initiation of liquid at 90°C. See (18).

640/19/309

"Effect of Cavitation on the Shock Sensitivity of Liquid Explosives," V. Krishna Mohan and J. Edmund Hay (BuMines), Seventh Symposium (International) on Detonation, pp 373-384, 1981.

Describes the gap test for cavitated liquids. Shock sensitization due to cavitation is observed for NM, the threshold shock pressure changes from 80 Kbars to 7 Kbars with cavitation added by air bubbles. Propagation velocity was about 2600 m/sec for cavitated liquid (uncavitated 6320 m/sec). Shock sensitivity is affected by the γ value of the gas with NM. Higher threshold values are obtained with argon ($\gamma = 1.67$) and the reverse for propane ($\gamma = 1.13$) compared to those observed with air and nitrogen ($\gamma = 1.40$). Threshold gap values are enhanced with oxygen (even though gammas are about the same as nitrogen and air). Diluents such as benzene or acetone desensitize NM at low diluent concentrations. Tests were done that demonstrated that "gas bubbles govern the initiation characteristics of NM." Vapor pressure of NM is given as 30 mm.

Wall has role in creating precursor, but also governs time that the dynamic pressure is maintained in the reaction zone, cavitating to driving reaction to completion.

JH: All the qualitative features are brought together. Need gamma for high vapor content of NM. Note threshold for shock initiation and detonation velocities given for LVD and HVD.

641/53/336

"Investigation of Detonations in Liquid Hydrazines," H. Beeson and M. Plaster, 1988 JANNAF Safety and Environmental Protection Subcommittee Meeting, Chemical Propulsion Information Agency, May 1988.

Provides a background with references on shock initiation of detonation, low velocity detonation and the role of "hot spots" or energy intensifiers in these processes. Quotes Watson that LVD requires higher sound velocity in container than in liquid and wall thickness above a minimum value. Describes a modified card-gap apparatus with a 2 inch diameter.

Hydrazine did not detonate with a donor charge of 0.49 lb of C-4. Damage consistent with an LVD in 0.5 inch tubes with 0.035 inch wall thickness was not observed (latter is below the 0.06 Watson criterion) was not observed.

Experimental results indicate that the explosive events observed in rapid compression experiments by Baker (52) involve more complex phenomena

than simple shock initiations. **JH: Baker stresses froth compression as key mechanism and considers physical kinetics of froth as control mechanism.**

642/55/352

"Sensitivity of Nitromethane for Low Velocity Detonation," R. R. Ljsselstein (Neth), Propellants, Explosives, Pyrotechnics, 10, 1, pp 14-17, February 1985.

Maps the shock loading regime in which a stable LVD can develop using a modified gap test (details given). Including LVD's, NM appears to have a sensitivity comparable to that of relatively sensitive high explosives. Explanation is that of Watson, with cavitation precursor. Threshold for heavily confined NM with a hollow axial tube for LVD is 1.5 GPa, HVD is 7 GPa (15 Kbars, 15,000 atm). The threshold and violence of an LVD explosion are strongly influenced by the dimensions, materials of the confinements, and presence of axial inclusions. ". . . under confined circumstances such as may occur for instance when it is pumped through pipelines nitromethane should be treated as a reasonably sensitive high explosive." **JH: The data in this paper are not for the conditions encountered in pumping through pipelines. The threshold for LVD far exceeds any water-hammer generated pressure. It may have value for fragment/plate impact or sympathetic detonation and for propagation of LVD instead of HVD regarding performance.**

Found the distance required to establish an LVD for the strong confinement used here (steel tube i.d. = 31.5 mm, o.d. = 63.5 mm) was 150 to 250 mm which means that test set-up requires a very long tube. (NOL large scale gap test is only 140 mm) or erroneous results may be inferred. The shock velocity of the stimulus may decrease to the sound velocity level before building up to the LVD value (1200 m/s).)

JH: The possibility that the initiation scheme in TEXS will produce LVD instead of HVD, greatly impairing performance, requires serious consideration.

643/56/351

"On the Low-Velocity Detonation of Nitromethane," A. A. Schilperoord (Netherlands), Seventh Symposium (International) on Detonation, pp 575-582, 1981.

Experimental work is described which shows that nitromethane is able to undergo a low-velocity detonation (LVD) reaction, if confined in a steel tube and subjected to a shock wave of appropriate strength. It is concluded that the occurrence of LVD in nitromethane requires such conditions as to enable both cavitation of liquid and sufficient explosive reaction. The latter condition means a rather strong confinement, because of the relatively low reaction rate of nitromethane. The results of this work may lead to an improved design of a gap test for the investigation of the shock wave sensitivity of liquids.

A stable LVD is characterized by a constant velocity higher than the sound velocity of the cavitated liquid.

Results explained by Watson theory. For NM, when sufficient confinement is available, its sensitivity is comparable to that of sensitive high explosives (~ 10 Kbars). **JH: Data is needed for the TEXS configuration; pipe not enclosed and also buried; and versus temperature.**

Dimensions of Steel Tubes with Identification (in mm)

Inner diameter	30	31	31	50	31.5
Outer diameter	35	38	51	70	63.5
Wall thickness	2.5	3.5	10	10	16
Length	750	750	750	750	750
Identification	30/35	31/38	31/51	50/70	31.5/63.5

LVD in 31.5/63 steel tube; marginal in 50/70 and 31/51 which have same wall thickness.

644/310/415

"Detonation in Homogeneous Explosives," A. W. Campbell, M. E. Malin, and T. E. Holland (LANL), Second ONR Symposium on Detonation, 1955.

Used NM in 55 gallon drums from Commerical Solvents specified as NM by weight minimum 95, Nitroparaffin 99, Specific Gravity 25/25°C 1.1283, Audity as acetic and 0.01, Water 0.052. "To further guard against the presence of alkaline materials which might act out as sensitizers to NM was redistilled at reduced pressure from sulfuric acid and stored in glass bottles." The temperature (°C) dependence of density given by $d_T = 1.1645 - 1.337 \times 10^{-3} T - 1.15 \times 10^{-6} T^2 + 3.8 \times 10^{-9} T^3$. Raising temperature increases detonation velocity **but** decreasing density decreases detonation velocity of T for liquid explosives. The combination results in NM in a decrease of -3.7 m/sec/°C with increase. Provides data on diameter effect in NM versus T in glass tubes and for the failure diameter. For latter, over the range -12°F to 98°F the failure diameter varied from 15 mm to 35 mm, increasing as the initial temperature was lowered. **JH: Thus for HVD below 1-½ inch at -12°F, failure to propagate would occur. For TEXS at low T limit, a construction to 2 inch diameter must be avoided.** "Plastic tubes were not used because of the possibility of contamination of the explosive by solvent action." **JH: Is this a problem with polyethylene tubes used for TEXS?** "Failure occurred by non-luminous areas spreading inward from the confining walls and choking off the detonation process." Provides test configurations for liquids for detonation velocity, diameter, and confinement versus temperature.

645/312

"Shock Initiation of Detonation in Liquid Explosives," W. W. Campbell, W. C. Davis, and J. R. Travis (LANL), Third Symposium on Detonation, 1960, and _Physics of Fluids_, 4, No. 4, pp 498-510, April 1961 (essentially the same).

"Nitromethane and other explosives in the homogeneous state are initiated as a result of shock heating. The initiation process is essentially a thermal explosion. The shock heated explosive reacts very slowly at first, but the reaction rate accelerates due to self-heating and detonation results. This detonation wave overtakes the initial shock wave and temporarily overdrives detonation in the unshocked explosive ahead of it." The induction time (between entrance of initial shock and initiation) varied from 5.0 microseconds at NM temperature of 1.7°C to 0.45 microseconds at 45.5°C. The shock pressure was about 90 Kbar. **JK: This is the definitive comprehensive paper, referred to by all on homogeneous detonation. Fortunately it was done on NM. Therefore, it has all forms of data on HVD of NM. It also gives the experimental procedures used and earlier references.**

Also investigated initiation of bubbles of various gases. Here, the major effect appeared to be shock wave interactions due to presence of bubbles; therefore, solid objects were also introduced into the NM. This area is better treated in later LANL and BuMines papers.

646/353

"Reaction Zone Measurements in High Explosive Detonation Waves by Means of Shock-Induced Polarization," R. R. Ljsselstein (Netherlands), _Combustion and Flame_, 66, pp 27-35, 1986.

NM was contained in a 100 mm long 28 mm inner diameter PVC tube. Uses shock induced polarization in confinement to monitor propagation and deduce reaction time and, therefore, reaction zone length. For NM at density 1.13 g/cm^3, reaction time is 27 nanoseconds and reaction zone length is 0.12 mm.

647 - 650

Reserved for future use.

"Detonation Waves in a Liquid-Gas Bubble System," A. I. Sychev, Combustion, Explosion and Shock Waves, pp 365-372, November 1985.

This author is coauthor in two more recent papers (75) and (77).

Describes equipment for creating a column of liquid containing bubbles and studying shock wave propagation including instrumentation used.

Referring to adiabatic compression by a shock wave, he notes that "if a bubble is not ignited upon compression before formation of a cumulative jet, subsequent ignition of the explosive mixture in the bubble is possible upon propagation of the liquid jet."

Regarding possible bubble interaction, he finds that the region of hot gas mixture explosion products in the bubbles does not exceed 6 d_0 while the mean distance between bubbles in the case photographed was 2.3 d_0. JH: A jet in a bubble occurs when the collapse is due to a planar shock on a spherical bubble. For compression due to slow rise of pressure, a spherical collapse is more likely. With bubble surface breakup also a possibility, but not formation of a Munroe jet.

652

"Measurements of the Shock Adiabatics of Cast TNT, Crystalline RDX and Nitromethane," V. S. Ilynikhin, P. F. Pokhil, O. K. Rozanov, and N. S. Shvedova (USSR), Translated from Doklody Akad Nauk SSSR, Vol 131, No. 4, pp 793-797, April 1960.

Describes what is now the standard method of measurement of shock Hugoniot by measuring the velocity of free surface (in contact with NM) of metal to be accelerated when shocks of various strengths are propagated through NM. For NM it gives equation $U = 2.0 + 1.38\ u$ km/sec where U is shock velocity and u is particle velocity. More precise measurements have been made at LANL and are quoted on page 599 of LASL Shock Hugoniot Data by Stanley P. Marsh, editor (University of California Press 1980) as $U = 1.65 + 1.64\ u$. The differences may in part be attributable to range covered and state of NM. JH: If shock Hugoniot of NM is needed, it is suggested a look at the LANL reference and a review of this one be done to understand the difference.

653

"Parameters of Supercompressed Detonation for Nitromethane and a Solution of Nitromethane with Bromoform," M. F. Gogulya and N. G. Demchenko, Combustion, Explosion and Shock Waves, July 1986.

Describes means of using flyer plate to overdrive the NM to achieve supercompression. A second method results from Mach stem formation (Mach disk). By placing a transparent region in contact with the NM one can

determine the temperature by optical means as long as transparency is preserved. Table I gives temperatures in the range of 3700 to 4600 K. Concludes that the temperature of the supercompressed detonation products (overdriven detonation) is connected to pressure by $T = 3700 + 16.32$ $(p - p_{cj})$ for NM when p_{cj} is the pressure at the Chapman-Jouguet plane in GPa (gigapascals). (To convert GPa to Kbar, multiply by 10.)

654

"Study of the Process of Initiation of Detonation of Explosives by Shock Waves Using the Method of Electrical Conductivity," A. N. Dremin and A. N. Mikhailov (USSR), pp 367-369. Translated from Fizika Gorenija i Vzryva, Vol 9, No. 3, pp 420-424, May-June, 1973.

Measures the shock initiation of pure NM as that of homogeneous liquid for 70-80 Kbar input. Does simultaneous measurement of electrical conductivity and optical observation of initiation process. Techniques are fully described. Results indicate that shock compression of NM decreases dielectric permeability. Asserts that the measurement of the dielectric permeability is the most sensitive method for determining the start of the transformation of a substance during shock compression.

CATEGORY 7

CHANGES IN NITROMETHANE

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"Heats of Combustion of Nitromethane and Dinitromethane; Enthalpies of Formation Nitroethyl Radicals and Energies of Dissociation of Bond in Nitro Derivatives of Methane," Yu. K. Kuobel', E. A. Miroshrichenko, and Yu., A. Lebedev, Izv Akad Nauk SSSR, Ser Khim, No. 3, pp 425-428, 1971.

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"Detonation of Nitromethane," B. N. Koudrikov, et al., Dokl Akad Nauk SSSR, 233, pp 315-318, 1977.

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"Thermal Decomposition of Aliphatic Nitro Compounds," G. M. Nazin, G. B. Manelis, and F. J. Dubovitskii, Uspekii, 37, pp 603-612, 1968.

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"Thermal Decomposition of Nitromethane in Shock Waves," J. S. Zaslonko, et al., Kin Katal, 13, pp 1001-1005, 1972.

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"Thermal Decomposition Reactions of Nitro Compounds. I. Dissociation of Nitromethane," K. Gläuzer and J. Troe, Helv Chim Acta, 55, pp 2884-2893, 1972, In German.

700

Summary of Category 7 - Changes in Nitromethane for Compendium of Nitromethane Data relevant to the Tactical Explosive System (TEXS) Program (with index to references on properties), Brigitta Dobratz, February 1989.

The behavior of NM, relevant to safe use in the TEXS program, can be affected by changes in handling, storing, and shipping conditions. These changes arise from interaction with other compounds/materials and time, pressure and/or temperature deviations from normal procedures.

The following time-, temperature-, pressure-, and material-affected characteristics were evaluated. In addition to papers dealing with a specific topic, several reviews and summaries are included (Ref. 701, 746, 747, 749, 768, 771, 775, 778, and 778).

In many of the experiments, data were obtained using only pure or purified NM (>99%); a few articles compare properties of pure NM with the commercial (impure) material (Ref. 727 and 744) and several give values for the commercial NM (Ref. 719, 720, 724, 728, 737, 738, 743, and 766). Characteristics of solid NM at low temperatures or high pressures are detailed in References 705, 708, 722, 731, 740, and 741.

Properties are given in handbooks as in References 502, 512/740, 514, 516/749 and in reviews and summaries, such as 521/745 and 523/775. Specific properties pertinent to TEX are listed below with the Angus value in parentheses.

Some researchers have derived equations that show dependence of the property on temperature and/or pressure. These are:

- Density - $\rho_{purif.} = 1.1615 - 1.1952 \times 10^{-3}t - 1.553 \times 10^{-6}t^2$

  $\rho_{unpurif.} = 1.1520 - 1.395 \times 10^{-3}t - 1.665 \times 10^{-6}t^2$ (Ref. 727)

  $\rho_{sat.liq.} = 1.1615 - 1.192 \times 10^{-2} - 1.553 \times 10^{-6}t^2$

  $\rho_t = 1.16448 - 0.001351t$ (Ref. 709)

  $\rho_{20° - 101°C} = 1.1668 - 0.001358t - 0.055t^2$ (Ref. 743)

- Melting point - mp - $T = 100 \ \ell nP + 389.2$, P in GPa (Ref. 729).

- Vapor pressure - $\log p = 10.8210 - 3905.39/(t + 260)$ (Ref. 727).

  $\log p = 7.2805 - 1446.186(t + 227.515)$, T = 328 to 409 K (Ref. 771).

- Heat capacity/specific heat - $C_p = 0.420 - 0.00076t + 0.060t^2$,

      t = 15° - 70°C (Ref. 743).

  $C_p = 0.397 - 0.00033t + 0.081t^2$,

      t = 30° - 70°C, C_{pmin} near 30°C

  (Ref. 743).

221

$$C_{pgas} = 0.0278 + 0.00078T + 0.00000044T^2,$$
$$t = 340 - 450 \text{ K and } p = 0.1 - 1.0 \text{ atm}$$
(Ref. 771).

$$C_{psat} = 104.44 + 6.3811 \times 10^{-2}t + 3.1753$$
$$\times 10^{-4}t^2 - 8.1318 \times 10^{-7}t^3 + 4.0739 \times$$
$$10^{-9}t^4 \text{ J/mole} - °C, \quad t = 35° \text{ to } 200°C$$
(Ref. 728).

$$C_p = 2.352 + 4.2882 \times 10^{-2}T - 1.694 \times$$
$$10^{-5}T^2 \text{ cal/deg. mole}, \quad T = 363.20 \text{ to}$$
$$523.25 \text{ K (Ref. 708).}$$

- Heat of vaporization - $\Delta H_v = 11730 - 4.9977T - 1.24 \times 10^{-2}T^2$, T = 318 - 374 K (Ref. 771).

- <u>Compatibility and Solubility</u>

The general topic and problems of compatibility are outlined and reviewed in Ref. 506 and 746.

After tests at room temperature and at 50°C, NM was found stable and noncorrosive with type 464 stainless steel, 2S Al, WD1010 cold-rolled steel, coating on steel. Impurities in commercial NM caused twice the pressure drop noted with pure NM in a glass vessel; they also tested positive with reagents (Ref. 711 and 744). NM reacts slowly with steel, Al, and Cu when wet (Ref. 749 and 774). Stable/compatible are bakelite, PE, chlorinated rubber (Ref. 774). Nitrite rubber reacts with NM (Ref. 777). NM tends to react with amines, strong acid, and oxidizers, and with alkalis (Ref. 747, 757, and 760).

NM is a dipolar aprotic solvent with high relative permittivity and weak electron-donor ability (Ref. 745). The solvent/solute properties of NM are compiled in References 747 and 748. Specifically, solubilities of NM vapor in olive oil and in H_2O were determined from ~0° to ~41°C and found comparable (Ref. 711). NM is also soluble in H_2O, ethanol, ether, acetone (Ref. 747). The solubilities of gases He, Ne, Ar, Kr, Xe, N_2, SF_6, and OsO_4 were determined and were slight except for OsO_4 (Ref. 742). NM is also used as solvent for cellulose acetate, acetobutyrate, and triacetate, dyes, fats, NC, oils, vinyls, alkyds, waxes, etc. (Ref. 748). Special caution must be exercised when distilling NM, because it can explode in mixtures with amines and alkalis (Ref. 750).

- <u>Physical Properties</u>

The relevant physical properties found in the literature and summarized below are: density (ρ), boiling point (bp), freezing point (fp), vapor pressure (vp), viscosity (η), sound speed (U), critical (T_c) and explosion temperature (T_x), volume compressibility (β), and surface tension.

ρ = 1.144 g/mL/5°, 1.141/15°, 1.138/20°, 1.128/25°, 1.124/30°, 1.113/35°C (Ref. 709, 710, 737, 738, and 770) (Angus 1.1382/20°, 1.1244/30°).

$\rho_{crit.}$ = 0.352 g/cm^3 (Ref. 717).

Density decreases linearly with increasing temperature (Ref. 738).

bp = 101.20°C at 760 mm (Ref. 710) (Angus 101.2°C)
bp = 99.98°C at 760 mm, 88.23° at 507.5, 74.25° at 315.52, 50.85° at 123.76 for 99.45% pure NM (Ref. 712).

fp = -28.55°C (Ref. 710) (Angus - 28.55°C).

$vp_{crit.}$ = 915 psia (Ref. 715) = 62.3 atm (Ref. 771).

vp = 16.12 mm/0°, 36.66/24.95°, 149/41/55.71°, 730/4/100°, 2020.0/136.404°C (Ref. 708, 735, 740).

η = 6.21 x 10^{-3} g/cm·s at 25°C (Ref. 706) = 0.646 cp at 20°C, 0.608 at 25°C, 0.574 at 30°C (Ref. 709). (Angus 0.61/25°C).

U = 1330 m/s (Ref. 707, 737, 738) = 1350 m/s extrapolated to 20°C (Ref. 770).

T_c = 588 K (Ref. 717, 770, 505) (Angus 315°C)

T_x = 354°C at 1 Kbar, 278° at 10 Kbar, 184° at 50 Kbar (Ref. 339).

Compressibility

β_{ad} = 48.5 x 10^{-12} cm²/dyne (Ref. 779)
β_{is} = 69.6 x 10^{-12} cm²/dyne

surface tension = 40.67 dyne/cm at 0°, 37.5 at 20°, 36.7 at 25°, 35.9 at 30°, 30.72 at 60°C (Ref. 709, 714).

• Chemical Properties

The following chemical properties have been summarized below: heat capacity/specific heat (C_p and C_v), heats of combustion (H_c), formation (H_f), and vaporization (H_v), entropy, enthalpy, activation energy (E), coefficient of thermal expansion (CTE), and thermal conductivity (k).

C_p = 25.48 J/mole-deg at 30°C, 25.68 at 40°, 26.36 at 70°, 26.87 at 90° (Ref. 728, 737) (Angus 25.76 at 30°C).
= 0.698 cal/mole-deg at 13.17 K, 25.28 at 297.12 (Ref. 740).

C_v = 17.8 cal/mole-deg (Ref. 737, 738).

C_v is difficult to measure, is generally calculated (Ref. 738).

$-\Delta H_c$ = 168.0 - 175.87 kcal/mole (Ref. 735, 759, 786) (Angus 169.3 at 25°C).

$-\Delta H_f$ = 19.3 to 21.28 kcal/mole (Ref. 735, 759, 786) (Angus 27.03 at 25°C).

$-\Delta H_v$ = 9147 cal at 298.10 K, 8883 cal at 318.30 K, 8120 at 374.44
(Ref. 708, 759) (Angus 8225 at bp).

Entropy = 0.1678 erg/deg/cm^2 (Ref. 714) = 65.73 cal/deg-mole at 1 atm
and 298.10 K (Ref. 740).

Enthalpy = 86.4 erg/cm^2 (Ref. 714) = 283 kcal/mole for $C-NO_2$ group
(Ref. 759).

E = 50 kcal/mole at 690-750 K, 43 at 750-1145, 35 at 1145-1270,
13 ± 7 at 1270-1460 (Ref. 715) = 84.0 kJ/mole (Ref. 776).

E = 50.5 kcal/mole for liquid NM and 90 kcal/mole for solid NM at
100 K (Ref. 784).

E decreases from 209 kJ/mole at 400 K to 38 kJ/mole at 1200 K
(Ref. 775).

CTE(α) = 1.22 x 10^3/deg (Ref. 737) (Angus 0.00122/°C).

k = 0.1170°F/ft at 110°-168°F (Ref. 726) = 34.7 x 10^{-6}cal/cm-s-deg at
126.0°, 38.8 x 10^{-6} at 149°C (Ref. 755).

- ## Decomposition

Summaries and reviews are listed in References 506, 701, 768, 775, and
788. Types of decomposition evaluated in some detail are catalytic, photo-
lytic, and thermal. Additives and catalysts to accelerate or inhibit disso-
ciation reactions are listed. The majority of papers in Category 7 address
this topic with a lack of unanimity regarding the reaction pathways and pro-
ducts, which are dependent on additives and impurities as well as on tempera-
ture and pressure, e.g., Ref. 729).

Additives

Toluene, cis-2-butane, and NO were decomposition inhibitors (Ref.
785).

DETA, EDA, DTBP, NaOH, $C_2H_4O_2$, amines, pyridine, DMFA, HNO_3, H_2SO_4,
$HClO_4$ act as sensitizers and increase decomposition (Ref. 719, 723,
724, 786).

Gases

O increased the decomposition rate and decreased the amount of HCN,
whereas CO_2 decreased decomposition and increased production of HCN.
NO increased decomposition slightly at pressures near 40 mm, not
lower ones. 25% diacetyl peroxide caused decomposition of 4% NM
after 10 mm at 250°C. ~36% NO_2 reduced decomposition by ~1/2. He,
N, or CH_2O had no effect (Ref. 704, 732, 765, 769, 773, 785).

Catalysts

Stainless steel increases reaction rate 40-fold (Ref. 702).

Basic metallic oxides catalyze the decomposition, acidic ones do not (Ref. 774, 775).

Cr_2O_3, Al_2O_3, NiO/Al_2O_3 increased reaction rates at 265°C. Decomposition leads to catalyst deactivation because C is deposited at high pressures. Fe_2O_3 lost its activity after 33% decomposition, Cr_2O_3 suffered no loss (Refs. 733, 734, 772).

Thermal Decomposition

Effect of O	(%)	t(min)	NM dec (%)	
	5	5	4.3	At initial pressure of
	15	5	4.9	18-250 psia and 355°C
	13	15	16.5	(Ref. 703,704). Large
	6	31	25.6	amounts of NO inhibit
	14	31	27	decomposition (Ref. 704).

Behavior is strongly affected by pressure, decomposition is complex (Ref. 719, 720, 730, 731, 739).

Photolysis (review Ref. 768)

UV radiation decomposed NM at ~3.5%/h, products were H_2 and CH_2O (Ref. 702, 723, 786).

After induction time of several ns, production of NO_2 seemed to increase linearly with time (Ref. 718).

NM decomposition varied from 10 to 0.5%/h at altitudes of 0 to 50 km (Ref. 736).
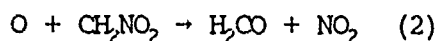
Reaction Kinetics

There seems to be a lack of unanimity regarding the decomposition reactions of NM (Ref. 701, 731, 761, 783, and others) and rate constants (k).

Reaction rates were 10^{-6} to 10^{-4} g-moles/s, $10^{-2.8}$ s^{-1} at 50 Kbar and 225°C (Ref. 720, 733).

Reaction rates are an indication of safety and stability under storage conditions. Preferred mechanisms are

$$O + CH_3NO_2 \rightarrow OH + CH_2NO_2 \quad (1)$$
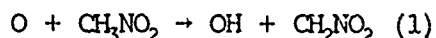
$$\Delta H_1 + \Delta H_2 = -460 \text{ kJ/mole (Ref. 766)}$$

$$O + CH_2NO_2 \rightarrow H_2CO + NO_2 \quad (2)$$

The initial step reaction was $CH_3NO_2 \rightarrow CH_3 + NO_2$ with k = 1.4 x 10^{-3} cm^3/mole-s at 700 K (Ref. 769, 780, 789).

225

The secondary process was much faster than the primary reaction (Ref. 721).

Photolysis reactions are $CH_3NO_2 + h\nu \rightarrow CH_3 + NO_2 \rightarrow NO_2 + h\nu \rightarrow NO + O$ and $CH_3NO_2 + h\nu \rightarrow CH_3ONO \rightarrow$ products (ref. 721, 736, 741).

At 292 K, reaction of NM vapors with O gave $k \sim 2 \times 10^{10}$ cm^3/mole-s, with CO 5.5×10^8 cm^3/mole-s (Ref. 752). At 295 K, the initial step rate was 1.9×10^6 cm^3/mole-s, secondary reaction $CO + OH \rightarrow CO_2 + H$ and $k = 9 \times 10^7$ cm^3/mole-s, (Ref. 759).

Dissociation energy of the C-N bond = ~53 kcal (Ref. 762, 764, 779).

Products

Decomposition products are dependent on temperature and pressure. Examples are given below:

HCN, NO, CO, CH_2O, CO_2, H_2O were identified at high pressure, HCN, NO, CO, H_2O, CH_4 at low pressure (Ref. 703, 704, 716, 768, 779).

Gaseous products from decomposition at 305°-440°C and 200-400 mm were NO, CH_4, and smaller amounts of C_2H_6, N_2O, C_2H_4 (Ref. 762, 763).

Brown fumes of NO_2 and a brown solid were seen (Ref. 716, 729, 731).

Products over catalysts were CO_2, NH_3, HCN, and H_2O, which increase with increasing pressure (Ref. 733, 734).

Products of pyrolysis were CH_4, NO_2, H_2O, NO, CH_2O, CH_3NO. Products of flash photolysis were free radicals CH_3 and NO_2, which undergo reactions with other products, eventually recombining to NM (Ref. 764).

For an explosion time of 10 s, the required temperature is 369°C at 1 Kbar, 327 at 10, and 225° at 50 (Ref. 720).

Comparison with catalytic decomposition shows that catalyst leads to lower temperature with activation energy of 35 kcal/mole versus 49.2 for uncatalyzed NM (Ref. 772).

701

"Nitromethane-Based Monopropellants," K. Seifert, et al., Acurex Corporation, Mountain View, CA, Final Report FR-80-45/AS, AFRPL-TR-81-17, May 1981.

This review summarized data on decomposition kinetics and catalysis. Additives were studied to reduce the adiabatic decomposition temperature to 3000°F. The reaction rates and kinetics are not known well enough to characterize the decomposition. Transition metal oxides and acetonates had been

tested to lower the activation energy for reaction. Internal heat operation speeds carbon deposition, but deposition decreased with aliphatic desensitizers. Metal oxides and acetonates were evaluated as decomposition catalysts.

702

"Research on Nitromethane," H. M. Kindsvater, et al., Aerojet Engineering Corporation, Azusa, CA, Final Report No. 493, AD-497957 (Dec. 1950), February 1951.

Thermal decomposition appears to be via a first-order reaction with an activation energy of 5.3 kcal/mole; a specific reaction rate k can be calculated for the equation $k = 1/t_{50}$ ($\ln$ 100/50), where t_{50} is the half-life found to be ~31 min at initial P ~ 72 mm Hg and T ~ 397 K; ~10 min at P ~ 150 mm Hg and T ~ 409 K. Hypergolic ignition was produced by addition of Na-K alloy; Li, Na, or K in conc. sol. of NH_3; also 3% solution of iron pantacarbonyl/chromic acid satur., chlorine trifluoride. Ultrasonic vibrations did not decompose NM, but high-intensity UV radiation caused decomposition of ~3.5% NM/h. The decomposition products had little effect on thermal sensitivity. Stainless steel is a specific catalyst for decomposition, increasing the reaction rate 40-fold. Major UV decomposition products are water and formaldehyde, which seem to have no catalytic properties. Experiments were conducted in all-glass apparatus.

BD: Recommend avoidance of alkali metal and SS contact as well as exposure to sunlight. NM obtained from Commercial Solvents was purified by distillation.

703

"Contribution of Chemical Reactions to a Time Lag in Nitromethane Rocket Motors," K. H. Mueller, Jet Propulsion, 25, pp 468-470, 1955.

Thermal decomposition was studied at 250 psia initial pressure and 355°C. The effect of O on decomposition was 5% O for 5 min - 4.3%, 14% O for 31 min - 27.0% NM decomposed at initial pressure 180 to 250 psia and 355°C. The main products were HCN, NO, CO, CO_2, H_2O.

704

"The Thermal Decomposition of Nitromethane at High Pressures," K. H. Mueller, ACS J, 77, pp 3459-3462, 1955.

Decomposition was studied at 355°C and 180 to 300 psia. Initial decomposition occurs by $CH_3NO_2 \rightarrow CH_3NO + O$ at high pressure and $CH_3NO_2 \rightarrow CH_3 + NO_2$ at low pressure. Relatively large amounts of NO inhibit decomposition. NM was obtained from Commercial Solvents and purified by steam distillation. Amounts and species of decomposition products was tabulated after 2, 5, 15, and 31 min and 24 h. Main products are HCN, H_2O, NO, and CO. CO_2 becomes significant as time elapses and pressure increases, whereas the other pro-

ducts decrease. During low-pressure decomposition, a 158 mm and 418°C for 28 min, the major products are HCN, NO, CO, H_2O, CH_4. Additions of NO and NO_2 were also studied. Their effects are: NO - small amounts do not affect the decomposition rate, but larger amounts seem to inhibit the reaction at high NM pressures. Addition of CO_2 did not affect the rate. NO_2 - CH_4 + NO_2 → CH_3NO_2 + H, CH_3NO_2 + NO_2 → CH_3O + NO + NO_2 → CO_2 + NO. The reaction of NM predominates, and the NO formed from the NO_2 addition leads to inhibition of decomposition. At high pressures, 40% NM leads to HCN and 10% to CH_4, 2% to C_2H_6. To account for 100% decomposition products the following decomposition reactions are suggested: CH_3NO_2 → CH_3NO + O, CH_3NO_2 + O → products; and CH_3NO_2 → CH_3NO_2 → CH_3 + NO_2, CH_3 + CH_3NO_2 → CH_4 + CH_3NO_2; CH_3 + CH_3 → C_2H_6.

705

"Refinement of the Structure of Solid Nitromethane," S. F. Trevino, E. Prince, and C. R. Hubbard, <u>J Chem Phys</u>, <u>73</u>, pp 2996-3000, 1980.

Single crystal x-ray diffraction analysis determined for NM are <u>ortho-rhombic structure</u> with space group $P2_12_12_1$. Atomic distances were determined at 4.2 K.

ED: This paper and others (Ref. 708, 722, and 731 are included because so little information is available on solid NM, and none on bulk material.

706

"Diffusion in Liquids," D. W. McCall, D. C. Douglass, and E. W. Anderson, <u>J Chem Phys</u>, <u>31</u>, pp 1555-1557, 1959.

The NM sample, from Amend Drug and Chemical Company, was redistilled. <u>Self-diffusion</u> coefficient was determined and <u>viscosity</u> given at 25°C. D = 2.11×10^{-5} cm^2/s, $\eta = 6.21 \times 10^{-3}$ g/cm-s.

707

"Temperature Coefficient of Ultrasonic Velocity in Solutions," G. W. Willard, <u>Acoust Soc J</u>, <u>19</u>, pp 235-241, 1947.

Single liquids have large negative temperature coefficients for 0° to 80°C. NM is n_D^{20} = 1.130, <u>solubility</u> - slightly soluble in H_2O, <u>velocity</u> 1330 m/s, temperature coefficient 3.0 (-ΔV/V/ ΔT x 10^3).

708

"Nitromethane: The Vapor Heat Capacity, Heat of Vaporization, Vapor Pressure and Gas Imperfection; The Chemical Thermodynamic Properties from 0 to 1500K," J. P. McCullough, et al., ACS J, 76, pp 4791-4796, 1954.

The sample, obtained from Commercial Solvents, was purified. v_p ranged from 149.41 mm at 55.711°C to 2026.0 mm at 136.404°C. ΔH_v = 883 cal at 318.30 K and 8120 cal at 374.44 K. C_p was determined from 363.20 to 523.25 K, and the following equation was developed: C_p = 2.352 + 4.2882 x 10^{-2} T - 1.694 x $10^{-5} T^2$ cal/deg-mole.

709

"The Purification and Some Physical Properties of Nitromethane," C. J. Thompson, H. J. Coleman, and R. V. Helm, ACS J, 76, pp 3445-3446, 1954.

The sample from Commercial Solvents was purified to better than 99.9% by successive washings and distillations. Properties were determined at 20, 25, 30°C: P_t = 1.16448 - 0.001351 t.

	20°C	25°C	30°C
density (g/mL)	1.13749	1.13064	1.12398
abs. viscosity (cp)	0.646	0.608	0.574
surface tension (dyne/cm)	37.5	36.7	35.9

710

"Physical Properties of Eight High-Purity Nitroparaffins," E. E. Toops, Jr., J Phys Chem, 60, pp 304-306, 1956.

NM was purified by fractional distillation, then properties were measured at three temperatures.

	20°C	25°C	30°C
density (g/mL)	1.13816	1.3128	1.12439
refractive index	1.38188	1.37964	1.37738

bp 760 mm (°C)	101.20
fp (°C)	-28.55
dt/dp (°C/min)	0.0427

711/503

"Handling of Nitroparaffins," C. E. Watts and W. C. Goinner (Commercial Solvents Company), Chem Engr News, 30, p 2344, 1952.

Toxicity: 100 ppm vapor in air. Precautions given for prolonged industrial exposure. Storage Stability: Completely stable under anhydrous conditions. Corrosion is inhibited by small amounts of phosphoric acid or monobutyl phosphate. Certain lead pigments cause pressure buildup in stored

cases, but with basic lead carbonate and lead sulfate are okay. Impact Stability: NM will explode when heated for 16.5 min at 605°F in tightly closed containers in air or N_2. Bullet impact causes detonation in heavy walled (0.25-in. steel) containers. Dry Salt Hazard: Nitroparaffins are slightly acidic in water due to nitronic acid. The acid forms salts with inorganic bases. The dry salts are explosive. Use of masks supplying fresh air is recommended. Hopcalite and activated-carbon-type respirators must not be used.

712

"Physical Data on Some Organic Compounds," R. R. Dreisbach and R. A. Martin, I&EC, 41, pp 2875-2880, 1949.

Physical properties of 99.45% pure NM are measured and agree with NBS bp values to ± 0.01°C. The p-bp data are: 760 mm - 99.98°C; 507.5 - 88.23; 315.52 - 74.25; 123.76 - 50.85.

713

"Olive Oil as a Solvent for Certain Organic Vapors," R. Macy and B. Genauf, Science, 106, pp 274-275, 1947.

Solubilities of NM in olive oil and water are compared at temperatures from 0 to ~40°C. Samples were 5 g in sealed glass tubes. NM and olive oil form a two-liquid system at 20°C when the NM mole fraction in the oil phase reaches 0.67 (interpolated from data in Table 2). At concentrations above ~0.2 mole fraction, the solubility of NM decreases to below normal.

BD: Normal seems to mean linear (no deviation from Henry's or Raoult's laws in Figure 1).

In olive oil		In water	
T (°C)	Conc	T (°C)	Conc
3.0	9.31	0.7	9.32
17.1	10.79	15.8	10.39
24.5	11.94	25.7	11.29
41.2	14.65	40.5	13.17

714

"Thermodynamics of Eight High Purity Nitroparaffins from 0° to 60°C," C. C. Snead and H. L. Clever, J Chem Eng Data, 7, pp 393-394, 1962.

Surface tension was measured at 10°C intervals on NM in ampules provided by Commercial Solvents. Entropy, enthalpy, and latent heat are also given: 0.1678 erg/deg/cm^2, 86.4 erg/cm^2, and 50.9 erg/cm^2. Surface tension: 40.67 at 0°C, 30.72 at 60°C.

715

"Shock-Wave Decomposition of Nitroparaffins, Part I. Mass-Spectrometric Study of Nitromethane Decomposition," J. N. Bradley, <u>Faraday Soc Trans</u>, <u>57</u>, pp 1750-1756, 1961.

<u>Thermal decomposition</u> was studied at 1145 to 1460 K. The reaction is first order over this range, but the activation energy decreases with increasing temperature. Decomposition becomes complex as it proceeds. Activation energy is ~50 kcal/mole over 200 min. The Matheson, Coleman and Bell sample was distilled into the system. The reaction mixture was 10/90% NM/Ar, pressure 6-10 mm, the shock being driven by 510-515 mm H. The low and high temperature Arrhenius data cannot fit on the same straight line, probably because the reaction proceeds below the high pressure limit for unimolecular decay as predicted by theory. Disactivation energy is:

E (kcal/mole)	T (K)
50	690-750
43	750-1145
35	1145-1270
13 ± 7	1270-1460

716

"The Thermal Decomposition of Nitromethane," L. J. Hillenbrand, Jr. and M. L. Vilpatrick, <u>J Chem Phys</u>, <u>21</u>, pp 525-535, 1953.

Commercial samples were purified and results analyzed by polarography. Brown fumes of NO_2 were seen. Both flow and static <u>decomposition</u> procedures were explored. Other products were CH_2O, CH_4.

717

"The Critical Point of Nitromethane," D. N. Griffin, <u>ACS J</u>, <u>71</u>, pp 1423-1426, 1949.

<u>Critical temperature</u> has been determined by several empirical calculational methods. This paper gives results of measurements of vapor pressures for 1.5 - to 3.5-mL samples in an 8.2-mL i.d. ss-bomb. Results are T_c = 588 K, p_c = 915 psia, and d_c = 0.352 g/cm^3.

718

"On the Photodissociation of Nitromethane at 266 nm," H. S. Kwok, et al., Int J Chem Kin, 13, pp 1125-1131, 1981. AD-A111316

Experiments were done on NM molecules in a collisionless molecular beam. Production of NO_2 seemed to increase linearly in time after an induction time of several ns. But NM does not <u>photodissociate</u> directly after excitation at 266 nm.

719

"Thermal Decomposition of High Explosives at Static Pressures 10-50 Kilobars," E. L. Lee, R. H. Sanborn, and H. D. Stromberg, Proceedings of the 5th Symposium (International) on Detonation, August 18-21, 1970, Office of Naval Research, ACR-184, pp 331-337.

The <u>decomposition</u> behavior is affected strongly by pressure. Material was supplied by Commercial Solvents. Addition of amines promotes the aci-form, nitronic acid. IR studies indicate that decomposition is complex, apparently not influenced by the aci-form.

BD: See also **(720)** and **(739)**.

720

"Thermal Decomposition of Nitromethane and Some Nitroalkanes at Static High Pressures of 1 to 50 Kbar," E. L. Lee, et al., Combustion Institute, Western States Section, Paper No. 72-10, 1972. AD-A039019

The <u>thermal explosion times</u> have been measured at 1, 10, and 50 Kbar between 160° and 380°. At constant pressure, the explosion time decreases as the temperature increases. At constant temperature, the explosion time decreases with increasing pressure. For a constant explosion time of 10 s, the required temperature is 369°C at 1 Kbar and 327°C at 10 Kbar, 225°C at 50 Kbar. From Arrhenius kinetics, the decomposition rate at 50 Kbar and 225°C is $10^{-2.8}$ 1/s, $10^{7.4}$ times faster than the C-N bond fission. The decomposition mechanism is not known. **BD:** See also **(719)** and **(739)**.

721

"Photofragmentation of Nitromethane in a Molecular Beam at 193 nm," N. C. Blais, J Chem Phys, 79, pp 1723-1731, 1983.

<u>Photolysis</u> under collision-free molecular beam conditions could quantify photodissociation. NM absorbs one photon at 193 nm and dissociates by the primary process $CH_3NO_2 + h\nu \rightarrow CH_3 + NO_2$; then $NO_2 + h\nu \rightarrow NO + O$. This secondary process is much faster than the primary one, and ~30% NO_2 dissociates.

722

"The Structure of Nitromethane at Pressures of 0.3 to 6.0 GPa," D. T. Grouer, R. R. Ryan, and D. Schiferl, J Phys Chem, 89, pp 2315-2318, 1985.

No chemical changes were found in X-ray and Raman studies of single crystals to 11.7 GPa. Cell volume varies asymptotically from <200Å^3 at 6.3 GPa to ~290Å^3 at zero pressure. Lattice constants are compared and extrapolated to low temperatures (4 K, 78 K, 228 K) and agreement is good.

723

"Importance of Enolate Acions in the High-Pressure Kinetics of Nitroalkanes and Nitroaromatics," R. Engelke, W. L. Earl, and C. McRohlfing, Int J Chem Kin, 18, pp 1205-1214, 1986.

The aci or enol form of NM is prevalent at high pressure (means tens to hundreds of Kbars). Pressure in the reaction zone of detonating NM ~ 150 Kbar. Addition of bases (dimethylenetriamine (DETA and pyridine) increase the detonation sensitivity of NM. Exposure of NM to UV light also has a sensitizing effect.

BD: **Light decomposes NM, so it needs to be stored in the dark.**

724

"Detonation Sensitivity of Liquid Nitromethane Doped with Methyl Nitrite," R. Engelke, W. L. Earl, and C. B. Storen, Propellants, Explosives, Pyrotechnics, 13, pp 189-19C, 1988.

Methyl nitrite is an important chemical species in the early stages of NM detonation, $H_3CNO_2 \rightarrow H_3CONO \rightarrow H_3CO + NO$. Methyl nitrite is a sensitizer for commercial NM, but not as effective as the aci-ion (Ref. 721). In fact, addition of methyl nitrite does not sensitize NM to detonation.

BD: **This can be applied to decomposition reactions, too.**

725

"Production of the Nitromethane Aci Ion by Static High Pressure," R. Engelke, et al., J Phys Chem, 92, pp 6815-6819, 1988.

At very high static pressure (≈2 GPa) higher concentration of nitronate, the aci-ion of NM is produced. This is an important species in catalytic decomposition. NM was used as received. Where exposed to a laser beam, liquid NM decomposed quickly at 293 K and ≈4.0 GPa, but not at 0.3 GPa.

"Studies of Thermal Conductivity of Liquids, Part I, Part II," B. C. Saliadis, J. Coates, AIChE J, 1, pp 275-288, 1955.

Statistical error for the values of thermal conductivities of organic compounds by this new method is listed as ± 1.50%. For NM, k = 0.1170 at temperatures 110-168°F, using an Eastman Kodak highest purity research sample. In Part II an equation for k was derived. $k = C_p U_s L$, where C_p is specific heat, U_s is sound velocity, ρ density, and L available intermolecular distance. The temperature coefficient to calculate k at other than 68°F is $dL/dt = 0.0055 \times 10^{-11}$ ft/°F.

"Density and Vapor Pressure of Nitromethane 26° to 200°C," H. A. Berman and E. D. West, J Chem Engr Data, 12, pp 197-199, 1967.

Samples were freeze-dried spectro grade NM, became colored above 40°C. Apparatus used measures with better than 0.1% precision.

$d$purified = 1.1615 - 1.1952 x $10^{-3}t$ - 1.553 x $10^{-6}t^2$; dunpurif = 1.1520 - 1.1395 x $10^{-3}t$ - 1.665 x $10^{-3}t^2$. $\log \rho_{purified}$ = 10.8210 - 3905.39/(t + 260); same for unpurified sample. Where analyses are:

	NM purif (mole %)	NM unpurif (mole %)
NE	0.5	2.6
NP	0.04	0.6
H_2O	0.02	0.04
unidentified	0.01	0.01
propanenitrile	–	0.4

The effect of 0.5 mole% of NE would change ρ at 25°C by 0.05%. Change in ρ with composition can be estimated from the differences between the densities of the purified and unpurified samples, which is ~3 mole%.

"Heat Capacity of Liquid Nitromethane from 35° to 200°C," H. A. Berman and E. D. West, J Chem Eng Data, 14, pp 107-109, 1969.

A Commercial Solvents Co. sample was used (analysis H_2O: 0.015 wt%, 0.051 mole%; NE <0.01 wt%, 0.008 mole%; NP <0.01 wt%, 0.007 mole% by GC; NE 0.4 mole%; NP 0.02 mole% by MS). Equation for C_p of NM saturated under its own vp is

$$C_{sat} \text{ (J/mole°C)} = 104.44 + 6.3811 \times 10^2 t + 3.1753 \times 10^{-4}t^2 - 8.1318 \times 10^{-7}t^3 + 4.0739 \times 10^{-9}t^4, \text{ between 35° to 200°C.}$$

At temperatures	30°C	40°C	70°C	90°C
C_p	25.48	25.68	26.36	26.87 cal/mole-deg

729

"Irreversible Reaction of Nitromethane at Elevated Pressure and Temperature," J. W. Brasch, J Phys Chem, 84, pp 2084-2085, 1980.

NM reacts at 150°C and 50 Kbar to give a dark colored product that is viscous or a powdery solid, ≤ 1μg formed. Also, the reaction proceeds only in the gaseous state, generates CO_2, and traces of amines seem to increase the rate.

BD: This is a decomposition reaction.

730

"Effects of Pressure on the Thermal Decomposition and Chemical Reactivity of HMX, RDX, and Nitromethane," G. J. Piermarini, S. Block, and P. J. Miller, Combustion and Detonation Phenomena, 19th International Symposium, Conference of ICT, June 29-July 1, 1988, Karlsruhe, FRG, paper 15-1 to 15-11.

Pressures to 7.1 GPa and temperatures to 583 K were used. Pressure tends to increase the chemical reactivity and thermal decomposition. Spontaneous explosion may occur at room temperature under pressure. Measurements were made in a diamond-anvil, high-pressure cell. Thermal decomposition is observed above 1.54 GPa and 433 K by brown solid residue, liquid, and gases. Analysis of the solid residue gave ammonia, formic acid or its salt and water as major products up to 7 GPa. Increasing pressure decreases the time to explosion, increases the decomposition rate.

BD: Such small-scale, high-pressure, high-temperature experimental studies are valuable to establish fundamental properties safely. Their applicability to large amounts of NM should be tested.

731

"Effects of Pressure on the Thermal Decomposition Kinetics and Chemical Reactivity of Nitromethane," G. J. Piermarini, S. Block, and P. J. Miller, J Phys Chem, 93, pp 457-462, 1989.

NM undergoes rapid thermal decomposition above 433 K and 1.54 GPa. Dark brown gases and residue result. M_p ranges from ~290 K at 0.4 GPa to ~430 K at 1.54 GPa; equation derived is T (K) = 100 $\ln$ P + 389.2, P in GPa. Single crystals grown from the liquid in the diamond-anvil, high-pressure cell, were observed to explode at room temperature if pressed rapidly to > 3GPa. Fraction of NM decomposed at 2 GPa after 1000 s is ~0.05 at 403 K, ~0.22 at 413 K, and ~0.26 at 423 K. Two reaction mechanisms are involved in thermal decomposition to 5 GPa, with positive pressure dependence; mechanism

1 operates < 4 GPa and T ≤ 403 K, mechanism 2 is dominant at all T at 5 GPa and at T ≥ 413 K at 4 GPa. Changeover seems to occur at 413 K. Mechanism 1 operates at ≤ 413 K and 2 GPa, but at T ≥ 413 K mechanism 2 or a mixture of 1 and 2 operate. A third mechanism operates at > 5 GPa. Each mechanism has its characteristic decomposition rate and generates its own set of decomposition products. These reaction mechanisms are very complex. Thermal decomposition occurs via a complex bimolecular mechanism.

732

"The Thermal Decomposition of Nitromethane," H. A. Taylor and V. V. Vesselovsky, J Phys Chem, 39, pp 1095-1101, 1935.

NM was fractionated from a Kahlbaum sample, bp 100.5° - 10°C. Studies were made from 390° to 420°C, yielding a convenient decomposition rate. Percentage increase in pressure during reaction was 130, independent of T and P. Addition of gases He, N, NO, CO_2, and O was studied regarding effect on NM decomposition. Only O led to a substantial change in decomposition/reaction rate.

733

"Decomposition of Nitromethane Over NiO and Cr_2O_3 Catalysts," J. B. Benziger, Combust Sci Tech, 29, pp 191-205, 1982. AD-A147862

Decomposition kinetics were studied at temperatures 100-300°C and pressures 1-60 torr. NM heterogeneous decomposition caused catalyst deactivation by carbon deposition. Measurements were made with GC/MS. Reaction rates of 10^{-6} to 10^{-4} gmoles/s were measured. Formation rates of reaction products over Cr_2O_3/Al_2O_3 at 265°C, CO_2, NH_3, HCN, and H_2O, increase with pressure (Fig. 3). NiO/Al_2O_3 behaves similarly. Activity decreases with time, and used catalysts are darker in color due to carbon deposition. BET analysis gave 100% decrease in surface area after 90 min at 265°C for both catalysts. In homogeneous gas-phase decomposition is a first-order reaction with C-N bond scission. NiO catalysts formed much more NH_3 and almost no HCN product, which makes this reaction more exothermic than with Cr_2O_3.

734

"A Mechanistic Study of Nitromethane Decomposition on Nickel," J. B. Benziger, Appl Surface Sci, 17, pp 309-323, 1984. AD-A128444

Catalysts are explored to facilitate and accelerate NM decomposition exothermically. Catalysts tended to deactivate due to carbon deposition, the rate decreasing with increasing temperature. NM seemed to adsorb molecularly at 250 K with high sticking probability up to near saturation on clean Ni surfaces. NM decomposed at 370 K, giving HCN and H_2 as primary desorption products and N_2, H_2O, and NH_3 as lesser ones. Recombination reactions occur at higher temperatures, 675-1000 K. On NiO catalysts, desorption should occur before decomposition, and decomposition resulted in catalyst deactiva-

tion due to carbon deposition at higher pressures. Increased surface oxidation increases the activation energy for decomposition. Decomposition decreases with increasing surface coverage.

735

"Thermodynamic Properties of Nitroparaffins," D. E. Holcomb and C. L. Dorsey, Jr., I&EC, 41, pp 2788-2792, 1949.

Heat of combustion was measured to calculate heat of formation. A Parr bomb was used. At 25°C ΔH_c = 175.87 ± 0.18 kg-cal/mole and ΔH_f = 21.28 ± 0.18 kg-cal/mole. Vapor pressures were determined from 0° to 100°C, 16.12 to 730.4 mm.

736

"Atmospheric Photodissociation Lifetimes for Nitromethane, Methyl Nitrite, and Methyl Nitrate," W. D. Taylor, et al., Int J Chem Kin, 12, pp 231-240, 1980.

Lifetimes were calculated as function of altitude from measured visible and UV photoabsorption cross-sections at 298 K. The lifetime of NM varies from 10 to 0.5 h at altidudes from 0 to 50 km. NM was purified Mallinckrodt spectral grade. Gaseous NM begins absorption of solar radiation at ~370 nm and has maxima at 275 and 197 nm. Photodecomposition occurs upon absorption of solar radiation. Main reaction is $CH_3NO_2 + h\nu \rightarrow CH_3 + NO_2$.

BD: Keep NM out of the sun.

737

"Coefficient of Thermal Expansion of, and Sound Speed through, Nitromethane and Four Bis(difluoramino)alkanes," B. O. Reese, et al., J Chem Engr Data, 15, pp 140-142, 1970.

The C_p and C_v equations have terms for sound velocity, U, and thermal expansion, α. NM was obtained from Commercial Solvents, with GLC giving 96.5% NM, 2.3% NE, and 1.2% NP, also 0.1% H_2O. Densities were determined at 5°, 15°, 20°, 25°, 30°, 35°C in g/mL: 1.155, 1.141, 1.138, 1.128, 1.124, 1.113. α = 1.22 x 10^3deg^{-1}, U = 1.30 x 10^5 cm/s, C_p = 25.4 cal/mole · deg, C_v = 17.8 cal/mole · deg.

738

"Heat Capacities of Liquids, Part II. The Heat Capacity at Constant Volume of Nitromethane, Trinitrotoluene, and Four Difluoramino Alkanes," B. O. Reese, et al., Combustion Institute, Western States Section, Meeting October 28-29, 1968, Paper WSS/CI 68-39.

NM from Commercial Solvents was used for the experiments, anal 96.5% NM, 2.3% NE, 1.2% NP, 0.1% H_2O. Density decreases linearly with increasing temperature, $\rho_{50} = 1.155$, $\rho_{150} = 1.141$, $\rho_{250} = 1.128$, $\rho_{350} = 1.113$, sound speed $U_{250} = 1.30 \times 10^5$ cm/s, $C_{v250} = 17.8$ cal/g $\cdot$ deg $= 41$ cal/mole $\cdot$ deg. C_v is difficult to measure and generally has been calculated.

739

"Thermal Explosion Times of Nitromethane, Perdenteronitromethane, and Six Dinitroalkanes as a Function of Temperature at Static High Pressures of 1-50 Kbar," R. Shaw, et al., Combust Flame, 35, pp 237-247, 1979.

For a constant thermal explosion time of 30 s, the thermal explosion temperature is 354° at 1 Kbar, 278° at 10 Kbar, and 184°C at 50 Kbar, decreasing with increasing pressure.

BD: See also (718) and (719).

740

"The Entropy of Nitromethane, Heat Capacity of Solid and Liquid Vapor Pressure, Heats of Fusion and Vaporization," W. M. Jones and W. F. Giangue, ACS J, 69, pp 983-987, 1947.

A 500-cc sample was supplied by Commercial Solvents Corporation, then purified by fractionation. C_p was determined from 13.17 K to 297.12 K, 0.698 to 25.28 cal/deg-mole. mp = 244.73 K, vp = 3.666 cm at 298.10 K, $\Delta H_v = 9147$ cal/mole at 298.10 K. Entropy of ideal gas at 1 atm and 298.10 K = 65.73 ± 0.10 cal/deg-mole.

741

"Photolysis of Nitromethane and of Methyl Nitrite in an Argon Matrix; Infrared Detection of Nitroxyl, HNO," H. W. Brown and G. C. Pimentel, J Chem Phys, 29, pp 883-888, 1958.

Photolysis was carried out at 20 K. Methyl nitrite CH_3ONO and CH_2O were identified as products. Changing the light source, changed the amount of CH_3ONO obtained. IR spectra and intensities are listed. Proposed reaction process is $CH_3NO_2 + h\nu \rightarrow CH_3ONO \rightarrow$ products. This does not suggest free-radical fragmentation as was proposed for pyrolysis.

742

"The Solubilities of Sulfur Hexafluoride in Water and of the Rare Gases, Sulfur Hexafluoride and Osmium Tetroxide in Nitromethane," H. L. Friedman, ACS J, 76, pp 3294-3297, 1954.

Room-temperature rare gas solubilities in NM were determined, and for SF_6 at lower temperatures. Solubilities of these gases in water saturated with NM were also determined. Average solubilities with ~3% accuracy are:

Gas	in NM	in NM-saturated H_2O	in H_2O-saturated NM
He	0.0175	0.0088	0.0167
Ne	0.0245	-	-
A	0.145	0.0317	0.140
Kr	0.380	-	-
Xe	1.14	-	-
N.	0.091	-	-
SF_6	0.377	0.0055	-
OsO_4	1100	-	-

743

"A Study of the Physical Properties of Nitromethane," J. W. Williams, ACS J, 47, pp 2644-2652, 1925.

Eastman Kodak samples were purified. C_p was determined from 15° to 65°C. For NM (dried with P_2O_5) C_p (30°-70°C) = 0.397 - 0.00033t + 0.081t^2.

NM (dried with $CaCl_2$) C_p (15°-70°C) = 0.420 - 0.00076t + 0.060t^2.

$\vdash$(20°-101°C) = 1.1663 - 0.001358t - 0.055t^2. Effects of drying agents were studied. C_p shows minimum wear 30°C.

744

"Chemical Propellants, Mononitromethane," F. Bellinger, et al , I&EC, 40, pp 1324-1331, 1948.

Three different samples from Commercial Solvents were tested: 1. commercial, 95% NM with NP, NE, H_2O, and $C_2H_4O_2$ in impurities; 2. as above with 96% NM; 3. commercial sample purified by fractionation. Densities and viscosities were determined at 10°, 25°, and 40°C.

T (°C)	95% NM (g/cm^3)	η (c_p)	96% NM (g/cm^3)	η (c_p)	100% NM (g/cm^3)	η (c_p)
10	1.1406	0.749	1.1414	0.750	1.1490	0.748
25	1.1204	0.625	1.1213	0.627	1.1287	0.625
40	1.1000	0.533	1.1009	0.534	1.1080	0.533

Catalysts were tested to aid/accelerate decomposition/detonation. Compatibility was tested at 50°C storage in glass vessels used in lacquer-lined steel drums. Impurities increased pressure drop and discoloration, and tested more sensitive than pure NM. Gasoline acts as desensitizer, as do DPP, methanol, and some acetates.

745/521

"Recommended Methods for the Purification of Solvents and Tests for Impurities: Nitromethane," J. F. Coetzee and T. H. Chang, Pure Appl Chem, 8, pp 1542-1545, 1986.

NM is a dipolar aprotic solvent with high relative permitivity and weak electron-donor ability. If nitronate ions are allowed to form salts in NM, especially with heavy metals, explosion will result. Impurities are identified and purification procedure given. Toxicity and Explosion Hazard: NM acts as moderate irritant when inhaled (threshold limit in air 100 ppm); forms explosion mixture above 7.3v/v% in air. Distillation is hazardous, especially when traces of bases and heavy metal ions are present. Dried NM may explode when adding fresh molecular seives. In purification of commercial NM, water is easily removed. Relatively high concentrations of homologs lower its density and increase its viscosity.

BD: Impurities can cause explosion, increase viscosity. Formation of nitronate salts in NM increases sensitivity. Fumes/vapors are moderately irritating when inhaled.

746

"Chemical Compatibility and Safe Storage Considerations for Process Systems Hazards Analysis," C. J. Dahn, J Hazardous Mater, 4, pp 121-127, 1980.

Compatibility problems are encountered mostly in manufacture and/or storage. Liquids are more easily contaminated by gases, liquids, and solids than are solids in chemical process. Problems in storage can be long term: decomposition with self-heating, biological degradation can be promoted by high heat and humidity in storage as can corrosion. DSC and TGA are good tools to use. Frank-Kamenitski equation is used to calculate critical temperatures from kinetics and thermodynamic properties which are supplied.

747/512

"Compendium of Safety Data Sheets for Research and Industrial Chemicals, Part III," L. H. Keith and D. B. Walters, Nitromethane VCH Publishers, Deerfield Beach, FL, pp 1240-1241, 1985.

NM is a toxic skin irritant. Symptoms may be dermatitis, pulmonary irritation, weakness, ataxia, convulsions, liver and kidney injury, nausea, vomiting, diarrhea. Federal standard is 100 ppm. Antidotes are listed for skin and eye contact, inhalation, and ingestion. Store in an explosion-

proof, dark area. Dispose of waste in sealed plastic bags. PVA gloves may give skin protection when handling NM.

Changes in NM – Soluble in H_2O, ethanol, ether, acetone; usual physical properties are listed. NM can react with amines, strong acids and oxidizers, and with alkalies.

BD: This information on data sheets would be useful to have available for emergencies in the lab, plant, and field. See also (516).

2-NP physical properties are listed. DOT classification is flammable liquid. Vapors are toxic and irritating to eyes, skin, and mucous membranes. Exposure causes headache, dizziness, nausea, and diarrhea. Threshold limit value (TLV) is 25 ppm. Rinse with water if exposed and breathe fresh air.

748

"The Handbook of Solvents," L. Scheflan and M. B. Jacobs, Van Nostrand, New York, 1953.

NM is used like NE as solvent for cellulose acetate, acetobutyrate and triacetate, dyes, fats, NC, oils, vinyls, alkyds, waxes, etc. Physical properties are also given.

BD: Obviously this makes NM incompatible with these materials.

749/516

"Hazardous Chemicals Data Book," G. Weiss, editor, Hoyes Data Corporation, Park Ridge, NJ, 1980.

Chemical and physical properties are listed. Listed as flammable liquid with TLV of 100 ppm. Vapor is irritating to eyes, nose, and throat, and liquid is harmful if swallowed. Fire hazard: Flashback may occur along vapor trail or explode if ignited in confined space. 2-NP has TLV of 25 ppm. Chemical and physical properties are listed, as is fire hazard.

BD: The information on data sheets would be useful to have available for emergencies in the lab, plant, and field. See also (747/512).

750

"Handbook of Laboratory Waste Disposal," M. J. Pitt and E. Pitt, John Wiley and Sons, Halstead Press, 1985.

Solvents, mixtures and their hazards are discussed. NM should not be distilled because it might explode. Mixtures with amines (e.g. methylamine, aniline, diaminoethane) and alkalis can form shock-sensitive explosives that detonate on impact or friction.

"Recent Developments in Nitromethane Based Explosives," Richard S. Egly (Comm Solv), Proceedings of the Symposium of Military Applications of Commercial Explosives, Defense Research Establishment, Valcartier, Quebec, Canada, pp 190-218, PA U-148-396, November 1972.

This is a survey paper. Table 2 has physical and thermodynamic properties. Two hazards: (1) nearby explosion and (2) confined burning of NM. The viscosity and surface properties of NM are such that even quite small gas bubbles will rise rapidly to the surface and break." Bubbles do coalesce. The preferred entrapping materials are small thin-walled, hollow gas filled bubbles—1.5% of microballoons suffices to make NM sensitive to a No. 8 cap and 2.5% to a No. 6 cap.

Freezing point given as -28.55°C or -19.4°F. Gives data on use of methylene chloride in NM as a freezing point depressant (p 204). 70/30 NM/NC has -40.8°C as freezing point. JH: **Supercooling must be considered.**

752 - 754

Reserved for future use.

755

"The Thermal Conductivity of Organic Vapors. The Relationship Between Thermal Conductivity and Viscosity, and the Significance of the Eucken Factor," R. G. Vines and L. A. Bennett, J Chem Phys, 22, pp 360-366, 1954.

Thermal conductivities were determined from 40° to 160°C, NM's at 126.0° and 149.0°C, 34.7 and 38.8 x 10^{-6} cal/cm·s·deg. Variation of conductivity with pressure was linear.

756

"Nitromethane-Zeolite Ignition," L. Bretherick, Chem Brit, 15, p 431, 1979, Chem Ind, 1979.

"Nitromethane-zeolite ignition. Sir, Details of an unexpected and potentially hazardous incident related to me at the recent ACHEMA meeting in Frankfurt may be of interest to your readers."

"Of a litre quantity of nitromethane dried and stored over molecular sieve, 750 mL was removed for use and the flask was kept stoppered for several weeks. When a other portion of freshly activated sieve was added

to the flask, the contents erupted and ignited. It seems likely that under the anhydrous conditions, unstable sodium aci-nitromethane was slowly formed from the zeolitic sodium ions in the sieve structure, and later decomposed violently in the exotherm arising from adsorption of nitromethane on the fresh portion of 10A sieve."

"In a wider context, the possibility of a molecular sieve slowly releasing or exchanging ionic species under virtually anhydrous conditions should be remembered when it is considered as a drying agent for ion-sensitive materials."

L. Bretherick, BP Research Centre, Sunbury-on-Thames, Middlesex TW16 7LN.

NM, dried and stored over molecular sieve for several weeks, reacted violently and ignited where the flask was opened, probably because Na-aci NM had formed slowly. BD: **Keep alkali metal away from NM.**

757

"Rate Constants for Reactions of Hydroxyl Radicals with Nitromethane and Methyl Nitrite Vapors at 292 K," J. M. Campbell and K. Goodman, Chem Phys Lett, 36, pp 382-384, 1975.

Mixtures of NM, NO_2, and CO were reacted in a black-painted reaction vessel. GC showed that NM could not interfere with the CO_2 yield. Test temperature was 292 ± 2 K. $k = (5.5 \pm 0.6) \times 10^8$ dm^3/mole·s. Also studied was reaction of O with NM vapors in a discharge flow system at 292 K, for which $k \approx 2 \times 10^{10}$ dm^3/mole·s.

758

"Reaction of $O(_3P)$ Aboms with Nitromethane Vapour at 295 K," J. M. Campbell and K. Goodman, Chem Phys Lett, 34, pp 105-108, 1975.

Vapor decomposition in a discharge flow system at 295 K had an initial step rate constant of $(1.9 \pm 0.3) \times 10^6$ dm^3/mole·s. The NM vapour was Eastman Kodak spectro grade. Addition of CO leads to one additional reaction of significant rate, $CO + OH \rightarrow CO_2 + H$, with $k = (9.0 \pm 0.7) \times 10^7$ dm^3/mole·s. CHO and NO_2 are surmised as intermediate products.

759

"Heats of Combustion and Molecular Structure, IV. Aliphatic Nitroalkanes and Nitric Esters," R. C. Cass, et al., Chem Soc J, pp 958-963, 1958.

Standard heats of combustion and ΔH_f are -174.4 and -22.2 kcal/mole, respecitvely. Enthalpy of gas-phase formulation is 283 kcal/mole for $C-NO_2$ group.

760

"Chemical Sensitization of Nitro Compounds," M. D. Cook and J. P. Haskins, Combustion and Detonation Phenomena, 19th International Annual Conference of ICT, 1988, Karlsruhe, FRG, Paper No. 85-1 to 85-8.

The effects of various additives on sensitization and decomposition of NM are studied. The compound and mixtures were tested in a modified NOL gap test. Additives were diethylene triamine (DETA), ethylene diamine (EDA), di-t-butyl peroxide (DTBP), benzoyl peroxide (BP), NaOH, $C_2H_4O_2$. Sensitization might occur through production of the aci-ion (nitronic acid) as postulated by Engelke (725) or by a free-radical decomposition mechanism. Amines form an H-bonded complex with NM. The C-N bond is weakened; therefore, the sensitization of NM can be explained by the ability of amines, acids, bases, and peroxides to form complexes, either through H-bonding or by charge transfer. This shock sensitivity of nitroalkanes decreases dramatically as the number of C-atoms increases.

Material	Perspex gap (mm)
NM	13
NM/5% NaOh	24
NM/10% C_2HO_2	18
NM/10% DTBP	~13
NM/BP sat	~18

761

"The Thermal Decomposition of Nitromethane," T. L. Cottrell, T. E. Graham, and T. J. Reid, Faraday Soc Trans, 47, pp 584-590, 1951.

Thermal decomposition was studied at 380° to 430°C by a static method. Between 200 and 400 mm, a homogeneous and approximately first-order reaction was observed with $k = 10^{14.5}$ exp (-53,600/RT)/s. The main products were NO, CH_4, CO, and H_2O, some CO_2, and small amounts of C_2H_6, N_2O, C_2H_4, all gaseous products. The dissociation energy of the C-N bond in NM is ~53 kcal. Concentrations > 10% NO tend to retard decomposition.

762

"Reactions of Nitroalkanes in the Gas Phase. Part 1 - Pyrolysis of Nitromethane," C. G. Crawforth and D. J. Waddington, Faraday Soc Trans, 65, pp 1334-1349, 1969.

Gas-phase decomposition was studied in the temperature range 305-440°C; it was found to be pressure dependent. The principal products are CH_4, CO, CH_3NO, N_2, NO_2, H_2O. The percentage pressure change corresponds to % NM decomposed over 305°-440°C. An induction period is followed by a positive pressure change below ~380°C. As the temperature is increased, the pressure change increases from 100% at 375°C to 130% at 440°C, then tends to decrease slightly above 440°C. Pyrolysis reactions are discussed.

BD: Such reactions and products will not happen under normal TEXS operating conditions, but personnel should be aware of what might happen at extremes.

763

"Thermal Decomposition of the Nitroalkanes," P. Gray, A. D. Yoffe, and L. Roselaar, Faraday Soc Trans, 51, pp 1489-1497, 1955.

Samples are from Eastman Kodak (pure). Pyrolysis was found to obey first-order kinetics, the activation energy of decomposition being quoted as 53.2 kcal/mole. Reaction products are CH_4, NO_2, H_2O, NO, and free radicals in He at 447° and 480°C. CH_2O is a major pyrolysis product with CH_3NO.

764

"The Photolysis and Pyrolysis of Nitromethane and Methyl Nitrite," J. M. Napier and R. G. W. Novish, Roy Soc Proc, A299, pp 317-336, 1967.

Flash photolysis yields CH_3 radicals and NO_2. These fragments undergo recombination and disproportionation reactions to four other products. When NO is added, NM is eventually reformed through intermediate and radical reactions. Light absorption results in photolysis, in isomerization. Results were recorded by gas-phase spectra. Pyrolysis was probably carried out at 500° to 1200°C. Product distribution is significantly affected by the experimental conditions.

BD: Light decomposes NM. Store NM away from light.

765

"Reactions of Free Radicals with Nitro Compounds and Nitrates," B. A. Thrush and L. F. Salter, University of Cambridge, England, Final Technical Report, March 1981.

The reaction of oxygen atoms with NM was studied in a discharge flow system. The initial attack involved abstraction of an H-atom. Activation energy was ~22 kJ/mole for the primary decomposition reaction. Although secondary (free radical) reactions could be exothermic. Decomposition is by free-radical chain mechanism. Reaction rates are an indication of safety and stability under storage conditions, but are usually fast beyond the first step. Reaction rates of 0.02-1.0 s and total pressures of 1-10 torr prevailed in these experiments with purified material. The preferred initial reaction mechanisms are:

$$O + CH_3NO_2 \rightarrow OH + CH_2NO_2$$

$$\Delta H_1 + \Delta H_2 = -460 \text{ kJ/mole}$$

$$O + CH_2NO_2 \rightarrow H_2CO + NO_2$$
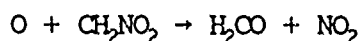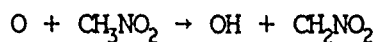
The Arrhenius parameters are $k_1 = 10^{(10.18 \pm 0.27)}$ exp(-22.4 ± 1.8 kJ/mole)/RT dm^3/mole·s.

Subsequent reactions are O + OH → O$_2$ + H, O + H$_2$CO → HCO + OH, O + HCO → CO + OH → CO$_2$ + H, H + HCO → H$_2$ + CO, O + NO$_2$ → O$_2$ + NO. Reactions of OH and NO$_2$ with O are fast, as is O + CH$_2$O.

766

"Influence of Impurities in Nitromethane on the Solubility of Some Metallic Salts. Attempts at Purification of this Solvent," J. C. Bardin, Analusis, 1, pp 140-144, 1972, In French.

Impurities in NM may form salts/complexes with metals. Propionitrile is particulary reactive and difficult to remove. We found fractional crystallization best to purify NM, but NM has little residual water. Aldrich < 5 · 10^{-3} M. Water forms hydroxides or hydrates with metallic cations. Propionitrile is present in concentration of 2 · 10^{-2} M and complexes strongly with Cu$^+$ ions; Ag$^+$, Hg$_2^{2+}$, Tl$^+$ behave similarly. Purity of NM is a critical factor because NM has great affinity to form mineral salts.

767

"On the Kinetics of Gas-Phase Thermal Decomposition of Nitromethane," C. Frejacques, C R, 231, pp 1061-1062, 1950, In French.

Experiments were done in a Pyrex Bourdon nanometer at 4 to 40 mm and 310° to 440°C. Experimental activation energies of the homogeneous reactions are:

E (kcal)	P (mm)
40	4
43	10
46	30

Influence of various gases was: N$_2$ and H$_2$O none; NO$_2$ little inhibition at low concentrations and accelerating for higher ones; O$_2$ accelerates the reaction but shows no catalysis for traces; H$_2$ decreases the decomposition rate almost proportionately to the molar ratio H$_2$/NM. Decomposition of free radicals of tetraethyl lead was achieved at 290°C.

768

"Photodecomposition of Energetic Nitro Compounds," J. C. Mialocq, J Phys Coll C4, Suppl, 48, No. 9, pp C4-163 to C4-178, 1987, In French.

The photodecomposition of NM depends on the excitation energy, light intensity. The review covers gas-phase, condensed-phase, and solution photolysis. Photodissociation proceeds in < 6 ps, i.e., very fast. Several reactions have been proposed as primary process.

769

"The Pyrolysis of Nitromethane. Part 1. Experimental Study: Nitromethane Alone and in the Presence of Additives. Part 2. Determination of a Simplified Mechanism, Bibliographic Review of Rate Constants. Part 3. Simulation of a Simplified Mechanism," A. Perche, J. C. Tricot, and M. Lucquin, J Chem Research, (S), pp 116-117, 304-307, 1979.

Decomposition can be explosive. The main decomposition products are NO, H_2O, CO, and CH_4 between 400° and 500°C. Effects of additives NO, NO_2, or CH_2O are insignificant on the concentrations of products. NO promotes decomposition slightly, CH_4 inhibits it. For the initial step, $CH_3NO_2 \rightarrow CH_3 + NO_2$, $k = 1.4 \times 10^{-3}$ $cm^3/mole \cdot s$ at 700 K. C-N bored scission leads to $CH_3 + NO_2$ in gas-phase decomposition.

770

"Ultrasonic Velocity in Some Organic Nitro- and Amino-Compounds," M. V. Kaulgud, Acoustica, 25, pp 22-27, 1971.

Measurements of sound velocities and densities are reported at temperatures from 30 to 100°C at 2 MHz. Both decrease linearly with increasing temperature. The sound velocity and density, extrapolated to 20°C are 1350 m/s and 1.138 g/cm^3.

771

"Thermodynamic Properties of Nitromethane," V. Ramaswanny, Indian J Technol, 14, pp 206-208, 1976.

Properties, to 1000 K and 100 atm, estimated were: critical constants, heat capacity, density, latent heat of vaporization, enthalpy, and entropy.

$P_c = 62.3$ atm $\quad T_c = 588$ K

$C_{p(g)} = 0.0278 + 0.00078T + 0.00000044T^2$, T = 340 - 450K, P = 0.11 to 10 atm.

$V_p = \log p = 7.2805 - 1446.186 \ (t + 227.515)$, T = 328 - 409 K

$H_v = 11730 - 4.9977T - 1.24 \times 10^{-2}T^2$, T = 318 - 374 K

$\rho_{(sat\ liq)} = 1.1615 - 1.192 \times 10^{-2}t - 1.553 \times 10^{-6}t^2$

772

"The Catalytic Decomposition of Nitromethane Under High Pressure," A. Hermoni (Makovky) and T. B. Gruenwald, 8th Symposium (International) on Combustion, Pasadena, CA, August 28 - September 3, 1960, Williams & Wilkins Co., Baltimore, MD, pp 1084-1088, 1962.

The high pressure decomposition of NM was studied in the presence of Cr_2O_3 and Fe_2O_3. The sample from Commercial Solvents was purified by distillation to bp = 101°C at 760 mm and n_d^{20} = 1.3818. NM and catalyst had to be kept separated in the test ampule because the catalyst is deactivated by contact with liquid NM. Decomposition kinetics was investigated at 220° to 245°C and initial pressure of 36 atm. No loss in activity was observed with Cr_2O_3 catalyst, but Fe_2O_3 lost its activity after 33% decomposition. Comparing the catalytic decomposition with thermal decomposition of NM without Cr_2O_3, it is noted that with catalyst NM decomposes at a lower temperature; has energy of activation of 36 kcal/mole versus 49.2; no HCN is evolved, but ammonium bicarbonate is a major product; the black solid obtained in small amounts is a major product in thermal decomposition. Two different reaction mechanisms are proposed. If O is injected with NM, the products of the thermal decomposition do not include HCN.

773

"The Thermal Decomposition of Nitromethane Under High Pressure," A. Makovsky and T. B. Gruenwald, Faraday Soc Trans, 55, pp 952-958, 1959.

The sample from Commercial Solvents was purified to bp = 101°C at 760 mm and n_b^{20} = 1.3818. Measurments were made at ~40 atm and temperature range 312-340°C, and indicate about first-order reaction. The main products of the decomposition reaction are H_2O, CO_2, HCN, NO, and CH_2O. Also, a solid of the formula $C_{10}H_{10}N_4O_2$ accumulated during the reaction. HCN generated increased with initial NM pressure. Adding CO_2, which increased the intial pressure, led to increased HCN production but decreased NM decomposition. Adding NO had no significant effect at low pressure and increased the decomposition rate slightly at pressures near 40 mm. Oxygen increases the decomposition rate of NM and reduces the amount of HCN. Addition of 25% diacetyl peroxide caused NM decomposition of 4% after 10 min at 250°C, where NM alone does not decompose at all. NO_2 retards the decomposition of NM, ~36% NO_2 reduces decomposition by ~half.

774

"Effect of Various Oxides on the Decomposition Temperature of Nitroparaffins," A. Hermoni (Makovky), and A. Salmon, Chem and Industry, p 1265, 1960.

Metallic oxides increase the sensitivity of NM to fire and detonation, probably as a result of a catalytic effect in air and in N. Basic oxides catalyze the reaction, acidic ones do not. The tests were carried out in a glass cup heated to a constant temperature on a hot plate. Three drops of NM were introduced into the cup, and the temperature at which rapid decompo-

sition started (the oxide becoming red in N or appearance of a flame in air) was recorded. From observations it is deduced that only the aci-form reacts with the catalysts.

BD: The test sounds as though it can serve as a screening test, even though the authors did not indicate the amount of oxide sample used.

Ignition temperatures (°C.) of nitroparaffins

Metal oxide	Nitromethane	Nitroethane	Nitropropane
$Co_2O_3+Co_3O_4$	70	70	70
PbO_2	90	90	90
Ni_2O_3	95	95	95
Cr_2O_3	115	115	115
Ag_2O	125		
ThO_2	175		
ZnO	180	180	180
MnO_2	185	185	185
Cu_2O	205	205	—
CaO	210	240	—
Cu_2O_3	210		
TiO_2	215		
PbO	215	no ignition up to 350°c.	
MgO	225	—	—
HgO	245	—	—
CdO	245		
Fe_2O_3	245	265	—
Al_2O_3	260	no ignition up to 350°c.	
CuO	265	285	285
CeO_2	295	—	—
Sb_2O_3	340	no ignition up to 350°c.	
V_2O_5 WO_3 P_2O_5	no ignition up to 350°c.		

775/523

"Nitromethane," A. Makovky and L. Lenji, Chem Reos, 58, pp 627-644, 1958. 776

Toxicity - NM is not significantly absorbed by the skin. When using respirators, do not use the activated-carbon type because of NM's high heat of adsorption. Hopcalite, used in respirators to convert CO to CO_2, affects NM to an extent that may cause fire. Thermal decomposition (Category 7) - Of gas additions tested, O_2 accelerates decomposition, H_2 slows it. Low-pressure and high-pressure decomposition mechanisms are described. Basic oxides catalyze the reaction, acidic ones do not. Photalysis reactions are also given. Additions of small amounts (trace to 2%) of a heavy metal (Cr, U, W) increased the explosion temperature from 312°C to 323.9°C, or 366.5°C. Corrosion rates are low; attacked are SS and Al alloys > 0.0001 in./yr and mild steel at ~0.0005 in./yr. Most other common metals and alloys are attacked at rates too low to cause structural failure. Resistant to attack are bakelite, chlorinated rubber, polyethylene, and 464SS. Water increases corrosiveness. Physical contants are tabulated.

776

"Decreasing Progression of the Decomposition Rate of Explosive Substances at High Temperatures," J. J. Janswonde and H. J. Pasman, Fast Reactions in Energetic Systems, Proceedings at NATO Advance Study Institute, Greece, July 6-19, 1980, pp 515-521.

Activation energy E(kJ/mole) = 84.0, and decreased with increasing temperature from 400 to 1200 K. The decrease in energy 209 to 38 kJ/mole is probably due to relative deceleration in the heat release caused by a reaction sequence of a primary endothermic dissociation followed by consecutive reactions producing the dominating heat effect.

777

"Influence of Structure on Polymer-Liquid Interaction. II. Influence of Nitrile Groups," G. Salomon, J Polym Sci, 3, pp 173-180, 1948.

NM interacts with nitrile rubber, causing swelling, which increases with temperature.

BD: This indicates a lack of **compatibility**. It seems advisable not to have pumping or storage devices made of nitrile rubber in contact with NM.

778

"Chemistry and Technology of Explosives," T. Urbanski, Pergamon Press, Vol 1, pp 579-587; Vol 3, pp 296-297, 1964.

The properties of explosives, including NM, have been reviewed critically and summarized.

779

"Thermal Decomposition of Nitromethane," A. A. Borisov, S. M. Kogarko, and G. J. Skachkov, Kin Katal, 7, pp 521-526, 1966.

The thermal decomposition and autoignition of NM vapors were studied at temperatures of 700 - 1300 K. The process obeys a first-order equation. At high pressures, 12-40 atm, HCN is a major decomposition product, explainable only by decomposition of CH_3NO. Main products are CH_4, NO, NO_2, HCN, CO, H_2O.

BD: These results seem more useful in explosion or ignition situations.

780

"Spectroscopic Investigation of the Decomposition of Nitromethane in Shock Waves," A. A. Borisov, J. S. Zaslonko, and S. M. Kogarko, Fiz Gor, 4, pp 222-227, 1968.

Decomposition was determined/studied above 1200 K. This method is limited by the large number of stable and intermediate products formed. An important intermediate in photolysis is CH_3ONO. The primary stage in decomposition is not known, but C-N bond rupture is assumed.

781

"Activation Energies of Monomolecular Dissociation Reactions from IR Spectroscopy Nitromethane," N. V. Chukairov, et al., Dokl Akad Nauk SSSR, Ser Khim Fiz, 277, pp 720-723, 1984.

The activation energy of dissociation depends on the length of the breaking bond, the C-N bond in this case. Calculated from spectral data were E = 50.5 ± 2 kcal/mole for liquid NM, 90 ± 12 kcal/mole at 100 K for solid, and 45 ± 2 kcal/mole for a dilute NM solution in CCl_4. The limiting activation energy for solid NM is twice that for the liquid, estimated but too small to be measured.

782

"Thermal Decomposition of Nitromethane," V. V. Dubikhin, G. M. Nazin, and G. B. Manelis, Izv Akad Nauk SSR, Ser Khim, No. 6, pp 1247-1249, 1971.

Formation of methane as a product of the thermal decomposition of NM is inhibited in the presence of NO. Decompositions were run at 360° and 390°C. The rate constant k for decomposition reaches a limiting value at 300 mm Hg.

783

"Heats of Combustion of Nitromethane and Dinitromethane; Enthalpies of Formation Nitroethyl Radicals and Energies of Dissociation of Bond in Nitro Derivatives of Methane," Yu. K. Kuobel', E. A. Miroshrichenko, and Yu., A. Lebedev, Izv Akad Nauk SSSR, Ser Khim, No. 3, pp 425-428, 1971.

Heat of combustion is 163.0 ± 0.3 kcal/mole and $\Delta H_{f9} = 19.3$ kcal/mole. Energies of dissociation of the C-N bond is estimated on the basis of available data as 60.3 kcal/mole; energies of formation of nitromethyl radicals were estimated as: CH_2NO_2 31.6, $CH(NO_2)_2$ 37.5, and $C(NO_2)_3$ 49.8 kcal/mole, and lead to energies of dissociation of the C-H bond in nitro derivatives of methane to ~103 kcal/mole.

"Detonation of Nitromethane," B. N. Koudrikov, et al., Dokl Akad Nauk SSSR, 233, pp 315-318, 1977.

NM is chemically active and forms nitronic acid, which is less stable than are the original substances. Commercial NM was distilled over P_2O_5 before the experiment. HNO_3, H_2SO_4, $HClO_4$, DMTA sensitized NM. Wrapping NM in their metallic foils, Sn, Ni, Cu, Al, did have little sensitizing effect. UV light effected some sensitizing action. Catalytic effect of bases on the chemical reaction rate during HVD was related to the effect of a strong shock wave.

"Thermal Decomposition of Aliphatic Nitro Compounds," G. M. Nazin, G. B. Manelis, and F. J. Dubovitskii, Usphekii, 37, pp 603-612, 1968.

The work on thermal decomposition is reviewed and summarized in this review.

"Thermal Decomposition of Nitromethane in Shock Waves," J. S. Zaslonko, et al., Kin Katal, 13, pp 1001-1005, 1972.

Experiments were performed in incident and reflected shock waves over 1030-1580 K and 1-2.8 atm. An induction period and weakly developed maximum of NO_2 absorption are noted. There is no induction period for decomposition at higher temperatures and NO_2 concentration decreases rapidly from the maximum with increasing temperature. Secondary reactions can increase NM consumption. The velocity constant is essentially independent of temperature, equal to ~2.5 x 10^9 L/mole·s.

"Intermolecular Free Lengths in the Liquid State. I. Adiabatic and Isothermal Compressibilities," B. Jacobson, Acta Cham Scand, 6, pp 1485-1498, 1952.

The molecules have closest packing density at 0 K, and the molar volume $V_0 = M/\rho_o$, where M is the molecular weight and ρ_o density at 0 K. The total surface of all molecules is designated Y in one mole. If the temperature is raised to T K, the liquid, not the molecules, is expanded. The available volume V_a at molar volume V_T at T K is $V_a = V_T - V_0$ and the free length L = $2V_a/Y$ when the surface is unaltered after a temperature rise. The adiabatic compressibility β is calculated from density ρ and sound velocity re as β_{ad} = $1/\rho\mu^2$ = 48.5 10^{-12} cm^2/dyne for NM and L = 0.44 10^{-8} cm. The isothermal compressibility β_{is} = $\gamma\beta_{ad}$, where $\gamma = c_p/c_v$, 69.6 10^{-12} cm^2/dyne and L = 0.44 cm^{-8}.

788

"Pyrolysis of Nitroalkanes in Shock Waves," K. Gläuzer and J. Troe, Recent Developments in Shock Tube Research, Proceedings 9th International Shock Tube Symposium Stanrord University, pp 743-748, 1973.

Reactions of dilute NM in Ar were studied in shock tubes. Calculated dissociation rate at 1100 K is 5.8 for the first-order reaction of C-N bond dissociation.

789

"Thermal Decomposition Reactions of Nitro Compounds. I. Dissociation of Nitromethane," K. Gläuzer and J. Troe, Helv Chim Acta, 55, pp 2884-2893, 1972, In German.

Thermal decomposition of dilute NM/Ar mixtures were studied at temperatures of 900 to 1500 K. Reaction times were 10^{-6} to 10^{-3} s at 2-20 atm. Simple dissociation of the C-N seems to occur at different pressures in the first step at high temperatures $CH_3NO_2(+M) \rightarrow CH_3 + NO_2(+M)$, $\Delta H = 58.8 \pm 0.2$ kcal/mole. The NO_2 reacts later as $NO_2 + CH_3 \rightarrow CH_3O + NO$.

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COMPENDIUM OF NITROMETHANE DATA RELEVANT TO THE TACTICAL EXPLOSIVE SYSTEM (TEXS) PROGRAM

J. Hershkowitz
B. M. Dobratz

April 1989

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A comprehensive search of the literature was conducted on nitromethane and hazards associated in its use. Each reference was reviewed and a summary provided. These summaries were grouped into the categories: adiabatic compression, detonation, tests, change in properties, health hazards, and problems associated with use in the Tactical Explosive System (TEXS). A guide to the use of the compendium and suggestions for research are included.

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